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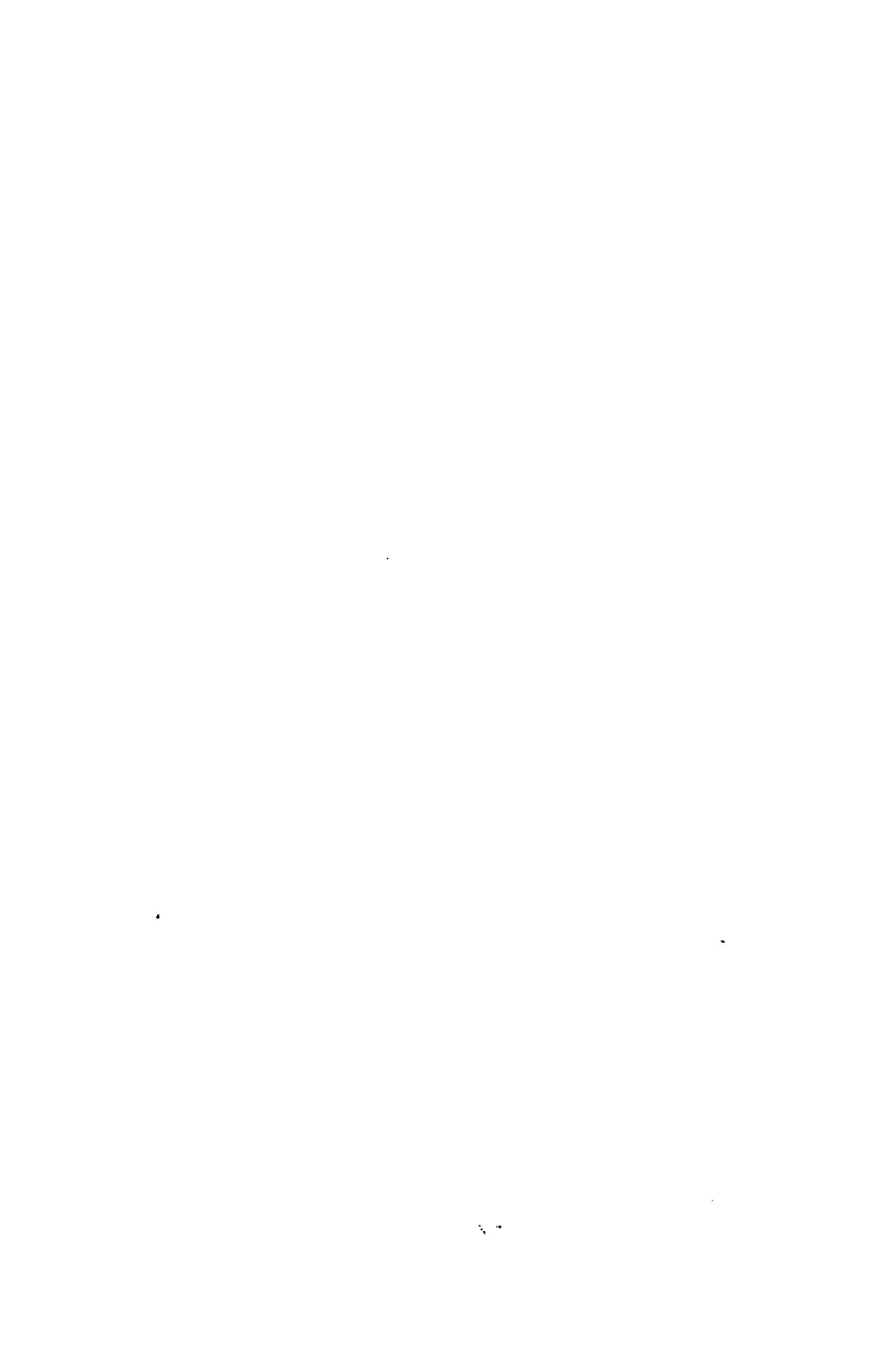


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AN
ESSAY
ON
CHEMICAL STATICS;
WITH
COPIOUS EXPLANATORY NOTES,
AND AN
APPENDIX
ON
VEGETABLE AND ANIMAL SUBSTANCES.

FAITHFULLY TRANSLATED FROM THE ORIGINAL FRENCH OF
C. L. BERTHOLLET,
MEMBER OF THE CONSERVATIVE SENATE, OF THE INSTITUTE, &c.
BY B. LAMBERT.

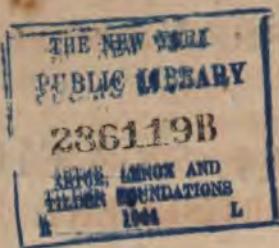
IN TWO VOLUMES.

VOL. I.

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ADVERTISEMENT.

THE known abilities of the illustrious Author of this Essay render any eulogium on its merits unnecessary; and the object of the Work is so ably set forth in his own Introduction, that the Translator can add nothing to it. It will be sufficient for him to observe that he has endeavoured to adhere closely to the Original, that the Author's meaning might be thoroughly comprehended; and that he has been induced to alter the arrangement of the Notes from a belief that they are more convenient for reference in their present situation, than when dispersed through the body of the work.



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INTRODUCTION.

THE powers which produce chemical phenomena are all derived from the mutual attraction of the moleculæ of bodies, to which the name of affinity is given, to distinguish it from astronomical attraction.

It is probable that they are the same property; but astronomical attraction being only exerted between masses placed at a distance, in which the figure of the moleculæ, their intervals, and peculiar habitudes, have no influence, its effects, in all cases proportionate to the mass, and in the inverse ratio of the square of the distances, may be the object of accurate calculation: the effects of chemical attraction or affinity are, on the contrary, so changed by particular and frequently indeterminate conditions, that they cannot be deduced

deduced from any general principle ; but must be considered in succession. There are but few of these effects which can be sufficiently disengaged from all the other phenomena to be rendered capable of precise calculation.

It is, therefore, by observation alone that the chemical properties of bodies, or those affinities by means of which they exert a reciprocal action in a determinate situation, can be estimated ; nevertheless, since it is very probable that affinity differs only in its origin from the general attraction, it ought to be also submitted to those laws which mechanics has established for the phenomena arising from the action of the mass, and it is natural to suppose that the more of generality there is in the principles from which the chemical theory is derived, the greater must be their analogy with those of mechanics ; but it is only by means of observation that they can attain to that degree which may be already foreseen.

The immediate effect of the affinity which a body exerts is always a combination ; hence all the effects produced by chemical ac-

are the consequence of the formation of some combination.

Every substance which has a tendency to enter into combination, acts in the ratio of its affinity and of its quantity. These facts are the ultimate end of every chemical observation.

But, 1st. The different tendencies to combination may be considered as so many forces which contribute to a result, or which partly destroy it by their opposition; these forces must, therefore, be distinguished in order to obtain an explanation of the phenomena which they produce, or to compare them together.

2d. The chemical action of a body does not depend solely upon the affinity peculiar to its component parts and upon the quantity; it also depends upon the state in which those parts are found, whether it be that of actual combination, which causes a larger or smaller portion of their affinity to disappear, or that, by their dilatation or condensation, their reciprocal distances are varied: it is these conditions which, by modifying the properties of the elementary parts of a substance,

INTRODUCTION.

stance, form that which I call its constitution: to obtain the analysis of chemical action, not only each of these conditions must be appreciated, but also every circumstance with which they have any connection.

The properties of bodies which can thus modify affinity have also other effects, independent of those which produce the combination, and which are the subjects of the different parts of physics. There are even many phenomena which, although they may be produced, wholly or in part, by affinity, ought nevertheless to be considered in another view, either because affinity contributes too slightly to their production, or because experiment has not hitherto been able to determine the particular affinities from which they arise. All those are called physical properties which do not seem to depend immediately on affinity.

Hence it follows, that a connection frequently exists between the physical properties and the chemical properties; that in many cases recourse must be had to both them for the explanation of a phenomenon to which they may each contribute, and t

it is necessary to establish an intimate relation between the different sciences of physics, that they may mutually elucidate each other.

The principles established on the results of facts observed under every point of view, and the explanation of chemical phenomena, founded on their relations to all the properties of which they are the consequences, constitute Theory, which should be distinguished into general theory and partial theories.

Some sciences may reach a certain degree of perfection without the aid of any theory, solely by means of an arbitrary order, established from the observations of those natural facts which are principally the subject of them; but this is not the case with chemistry, in which the observations ought, in almost every case, to arise from experiment alone, and in which the facts result from the factitious union of the circumstances from which they must be produced. In making an experiment it is necessary to have some object in view, and to be guided by an hypothesis; and to obtain any advantage from the observations, they must be compared under certain

certain conditions, and, at least, some of the circumstances necessary to the production of every phenomenon observed, must be ascertained, to the end that they may be reproduced. Thus, suppositions more or less illusory, and even those chimeras which at present appear ridiculous, but which have employed the most laborious investigations, were necessary to the infancy of chemistry: by their means facts were multiplied; a great number of properties were ascertained, and many arts were brought to perfection.

Still Chemistry was only enlarged with incomplete remarks and partial theories, unconnected with each other, which arose in succession like the caprices of the imagination, and had no relation to any general law; arrogant and insulated from every other species of knowledge, the greater the number of acquisitions made to it, the further was it removed from the character of true science.

It is only since the period that affinity has been recognized as the cause of all combinations, that Chemistry could be regarded as a science which began to have general principles: from that time its object has be-

bring the succession of combinations, which different elements are capable of forming, into a regular system, and to ascertain the proportions which enter into these combinations.

Bergman extended the application of this first principle very considerably: he pointed out the greatest number of the causes which might disguise or produce variations in its effects: on it he founded the processes of different chemical analysis, which brought it to a degree of precision unknown before his time.

A great number of phenomena, however, are dependent on the combination of oxigen, which, of all substances, is that whose affinities appear to be the most active, and its existence was not even known: hypotheses were, therefore, substituted for the action which it exercises. Priestley had no sooner made known this substance, which performs so important a part, than Lavoisier ascertained its combinations, and ascribed the numerous effects produced by it to the true cause. The great light spread by his immortal discoveries, not only over those phenomena

mena dependent on them, but also over the action of many other gases discovered at the same period, obtained, for the revolution which it produced, the honour of being regarded as a new and general theory.

The accurate investigation of a cause, equally powerful from the modifications produced by it in the results of affinity, that of the action of heat, was also necessary to explain the greater number of phenomena: it is to Black that the discovery of the fundamental properties of heat are due; since his time they have engaged the attention of many philosophers; but they were reduced to well-defined laws in an intelligent Memoir, for which we are indebted to Laplace and Lavoisier.

It is therefore evident that Chemistry has acquired, in our time, the knowledge of those generative properties which accompany all chemical action, and which are the source of all the phenomena produced by it: this science has therefore been founded upon principles which have been rapidly applied to every branch of knowledge within compass.

As the partial theories are limited in their researches to certain facts, or to some classes of phenomena, they may frequently be restricted to the rigorous application of some well ascertained properties, and may be said to be the cautious language of experience, until the progress of the science gives them a more enlarged extent: they may then be reduced to that certainty which belongs to knowledge founded on the testimony of our senses: this is particularly true with respect to the determination of the elements of a compound substance, and the means by which that determination is obtained.

This is not the case with a theory which comprehends the consideration of all the partial theories, and which aims at disentangling that which may belong in common to the chemical properties of all bodies, from that which depends on the particular qualities of each: employed in elucidating all the objects; in bringing to perfection all the processes; in collecting and comparing all the results, it endeavours to discover every power of each cause, and every cause which contributes to each phenomenon; it carries the mind

different substances? what are the forces which arise from their action in the effects produced by them? and, what are the properties of the forces which contribute to these effects, or which are in opposition to them?

The Essay is divided into two parts: in the first, I consider all the elements of chemical action; and, in the second, the substances which exercise it, and which contribute the most to chemical phenomena, classing them according to their habitudes, or the relations existing between their affinities.

The first effect of affinity, to which I call the attention, is that produced by the coherence of the particles which enter into the composition of a body; it is the effect of the reciprocal affinity of these particles, which I distinguish by the name of the force of cohesion, and which becomes a force opposed to all those tending to cause them to enter into another combination, while it, on the contrary, tends to re-unite them.

Every affinity which tends by its action to diminish the effect of cohesion ought to be regarded as a force opposed to it, and of which the result is solution. When, there-
fore

fore, a liquid acts on a solid, the force of solution can produce the liquefaction of the solid, if it is superior to that of cohesion; but this effect sometimes takes place immediately, and sometimes it requires that the cohesion should be first weakened by a commencement of combination; there are circumstances in which the liquid can only act on the surface of the solid and wet it; finally, the solid cannot even be wetted when its affinity with the liquid does not produce an effect greater than that of the mutual affinity of the parts of this latter. These two forces, therefore, according to their relations, produce different results, which must be distinguished, but which are not to be attributed, in conformity to the opinion of some philosophers, to two affinities, one of which they have considered as chemical, and the other as derived from the laws of physics.

The effects of the force of cohesion could not escape the attention of Chemists; but they have only considered it as a quality of bodies actually solid, so that when the solidity ceased they thought it was destroyed: on the contrary, its effects may cease to be

sensible without ceasing to act, which is also the case with all the physical powers comprehended in it: this is one of the principal causes of the difference to be found between the explanations I offer and those which have been adopted, and into which this consideration has not been admitted.

The reciprocal action which tends to unite the parts of a substance may be overcome by a dissolving power, and its energy diminishes in proportion as the quantity of the solvent increases, or as its action is assisted by heat; on the contrary it augments if the preceding circumstances are weakened, and finally reproduces the effects which are due to its preponderance: from this proceed all the separations and precipitations which take place in a liquid, and which arise from the formation of a solid.

Crystallization is one of the remarkable effects of the force of cohesion; the parts which crystallize assume a symmetrical arrangement which is determined by the mutual action of the small solids separated by their force of cohesion from a liquid: and the qualities of a solid which is more easily broken in one way than

than in another; which is more or less brittle, more or less elastic, more or less ductile, depend on this arrangement.

The different degrees of solubility of salts which arise from the relation of their force of cohesion to the action of the dissolving liquid, is not only the cause of their crystallization, but also of their successive separation by evaporation ; it is not only opposed to the effect of the solvent, but also to their mutual action ; because while the different salts are in solution, they form but one liquid, in which each peculiar action is counterbalanced until the force of cohesion of those which are least soluble has acquired sufficient energy to cause them to pass into the solid state.

Since the immediate effect of every chemical action is a combination, dissolution itself is only a combination considered with respect to the force of cohesion ; because in every combination it will be observed that the action of any substance is always in proportion to the quantity contained within the sphere of its activity : an immediate consequence of this law is that the action of a substance

stance diminishes in proportion to the saturation it experiences.

Among the affinities of a substance, there is frequently one which is predominant, and which gives the character to its distinctive properties: these are the energetic affinities which are useful in the classification of bodies in a system of chemistry, and which give birth to the greatest part of the chemical phenomena.

All the properties derived from this governing affinity become latent and re-appear with it; combination communicates new ones which have no longer any relation with those that the saturation has caused to disappear, but are the consequence of the changes produced by the condensation or by the dilatation of the elements of the combination; for the reciprocal action of the moleculæ of a combination is proportionate to the condensation or dilatation which brings them together or removes them from each other; thus, salts, in a state of combination, possess a peculiar solubility and crystallization.

Whenever those substances, in which a predominating

dominating affinity exists, undergo a combination foreign to the action of this affinity, they carry with them all the properties dependent on it, which are only modified by the constitution they have acquired and by the degree of saturation they have experienced; thus an alloy retains the metallic properties, and those which arise from the reciprocal action of the moleculæ, whether they are simple or compound, such as the force of cohesion, fusibility, as well as specific gravity, undergo a change which is only produced by that of the mutual distances of the moleculæ in that constitution which they have acquired by the combination.

A predominant and energetic affinity in one body, supposes an analogous disposition in some other substance, whose characteristic properties ought, from thence, to be considered as opposed to those of the first, since they cause them to disappear by saturation.

The acids and alkalis offer the most striking examples of these adverse properties which are the principal source of chemical phenomena; their reciprocal action, therefore, is deserving of the most particular attention.

In

In the first place I consider this co-relative property of the mutual saturation of acids and alkalis, as a general attribute, independent of the particular affections of each of them, and of the properties arising from the elements of which they are composed.

As this reciprocal saturation of the acids and alkalis is an immediate effect of their reciprocal affinity, it ought to be regarded as the measure of their affinity, if the respective quantities which are necessary to produce this effect are taken into consideration. From whence it follows that the affinities of the acids for the alkalis, or of the alkalis for the acids, are proportionate to their capacity for saturation. In consequence I maintain that whenever several acids act upon one alkaline base, the action of one of the acids does not overpower that of the others, so as to form an insulated combination, but each of the acids has a share in the action proportionate to its capacity for saturation and to its quantity : I call this compound result by the denomination of a *chemical mass* : hence I affirm that each of the acids which is found in combination with an alkaline base acts in the ratio of its

its mass ; and to ascertain the masses I compare the capacities for saturation, either of all the acids with a base, or of all the bases with an acid.

To explain the combinations which are formed by the operation of two acids on one base, and of those produced by the action of two acids and two bases, an elective attraction has been supposed, which, by its graduation, substitutes one substance for another in a combination, and which, in the reciprocal action of four substances, determines two combinations insulated from each other.

This supposition does not coincide with the general law of combinations ; but the consideration of the two distinct effects of affinity, in so far as it produces combinations, and is the principle of the force of cohesion, appears to me sufficient for the explanation of all the facts which are attributed to elective affinity and the action of the double affinities.

That general law to which chemical action is subjected, that substances act in the ratio of the energy of their affinity and their quantity, is not modified by the effects arising from the force

force of cohesion alone, but also by the expansive power of caloric, or the cause of heat, which is the principle of expansibility.

Since the action of every body is influenced by caloric, which consequently contributes to every chemical phenomenon, it is of importance to ascertain its general properties with precision, and the effects it produces under different conditions. On this subject, I shall enter into elementary details which may appear foreign to the end I have proposed.

The tendency of every substance to the solid, liquid, or elastic state, depends on the relation of the reciprocal action, by which the moleculeæ of a simple or compound body are disposed to unite, with the expansive action which caloric exercises upon them : the effect of caloric may, according to the circumstances, contribute to the combination of that substance with others, or it may be an obstacle to it. When caloric produces a state of elasticity, the gas arising from it must be considered as owing to the combination it forms, and the elasticity as an opposing power, either to solidity or to liquid combinations ; but the observation

have acquired and can communicate to their combination, regarding the affinity of this latter, as a power resulting from the elementary affinities which succeed it when the combination is at an end, or which give rise to other resulting affinities, when the state of the combination is changed.

All the phenomena of nature take place in the atmosphere, which frequently contributes to produce them by its compression, its temperature, or the combination of the parts which compose it ; an exact knowledge of the qualities of the atmosphere under these three relations, is therefore necessary.

The result of the different causes, which interpose during chemical action, is sometimes a combination whose proportions are constant ; sometimes, on the contrary, the proportions of the combinations which are formed, are not fixed, and vary according to the circumstances under which they are produced : in the first case, it requires an accumulation of powers to change the proportions equal to those which tend to maintain their state of combination ; this obstacle overcome, chemical

cal action continues to produce its effects in the ratio of the energy of the affinities and the quantity of the bodies which exercise it. I have endeavoured to ascertain the conditions which thus limit the proportions, in some combinations, and which appear to place an obstacle to the progress of chemical action.

There is still a condition in chemical action which must be taken into consideration and which affords an explanation of many of its effects; it is the interval of time which is necessary for its being performed, and which is very variable according to the substances, and according to the circumstances. I examine under this head the propagation of chemical action.

Having thus gone through all the known elements of chemical action, I proceed to the second part which is appropriated to the consideration of the nature of those substances which are most remarkable for their chemical properties, and are classed by their distinctive character or by the predominating affinity. I endeavour to find in their properties the origin of those of the combinations which they form,

form, according to the state in which they are found, and the explanation of the phenomena to which they contribute.

In this manner I examine the properties of inflammable substances; those of their mutual combinations; those of compound acids and of the different combinations derived from them, according to the proportions of their elements; those of the alkalis, the earths, and, finally, metallic substances.

Vegetable substances and animal substances are very complex, not so much by the number of the elements which enter into their composition, as by the substances which arise from them, and which all act by a resulting force; they are so unsettled and so variable that it is very difficult to obtain an exact knowledge of the causes of the phenomena arising from them; the greatest circumspection is necessary in considering them: I shall confine myself to indicating what appears to me to be best ascertained, or what may be most reasonably conjectured respecting the phenomena of this description, which chemistry has been able to attain.

Great

Great inequality will be found in the discussions into which I enter: I pass rapidly over some subjects of importance, but which offer no incertitude to chemists, and I dwell with much minuteness on others which appear to me to require new elucidations.

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ESSAY
ON
CHEMICAL STATICS.

PART THE FIRST.

OF CHEMICAL ACTION IN GENERAL.

SECTION I.

Of the Chemical Action of Solids and of Liquids.

CHAP. I.

Of the Force of Cohesion.

1. CHEMICAL action produces different effects, according as a substance is in a gaseous, liquid, or solid state, so that all chemical action is only a simple effect of affinity; but it is modified by the constitution of the body which exercises it: it is therefore important to discover the causes of chemical phenomena; to ascertain what may govern the constitution of substances; and what differences may produce each of its conditions, whether it precedes or whether it becomes

VOL. I.

B

a result

Great inequality will be found in discussions into which I enter: I have over some subjects of importance, which offer no incertitude to chemists, and which with much minuteness on one side, are opposed to it; to me to require new efforts.

Having a diminution of temperature, proves that their particles.

Integrant particles are subject to cohesion, as well as to similar: sulphate of barium, for instance, assumes a state of combination, as well as the parts of

number of liquid substances take a solid form, whenever the effect of the liquidity is diminished by a reduction of the temperature; thus water congeals and forms crystals, and there can be no doubt that a similar effect would take place on all liquids, if a sufficient degree of cold could be produced; but in this respect a great difference is observed between them.

Even the gases show this disposition in their particles: the oxygenated muriatic (acid?) gas becomes concrete, and crystallizes at a temperature near to that at which water congeals; and all the gaseous substances, when they have lost their elasticity, by forming a combination, are disposed to

solid state, if the temperature allows ammoniacal gas and carbonic acid to become solid as soon as they enter into contact with hydrogen gas, the most subtle of all fluids which can be retained in vessels, with oxygen gas, the water which forms concrete.

Doubt can therefore exist, that all the parts of every substance possess a uniform disposition to unite and form a solid body: if this effect cannot be produced, it is because the force of cohesion is overpowered by the action of caloric.

3. Although the effects of heat and the properties of caloric ought to undergo a particular analysis, it will nevertheless be necessary, in what follows, to consider the dilatation it produces on all bodies: this expansive power is not only in opposition to the force of cohesion, but also to the tendency which substances have to combine with each other, although, by its effects being opposed to those of other powers, it frequently happens that it is favourable to these combinations.

4. The force of cohesion, whether it be that which unites similar particles, or that which operates a combination, increases in a substance in proportion as its moleculeæ are brought nearer together; alumine which, after having been submitted to an elevated degree of heat, has shrunk considerably in bulk, has not only experienced much mechanical cohesion, but has acquired the

power of resisting acids and alkalis: the sapphire, which is little more than pure alumine, and whose cohesion may be compared to that of alumine which has experienced the greatest degree of heat, is not attacked by the most powerful agents, until that cohesion has been in a great measure destroyed: adamantine spar or corindon, which is scarcely any thing but alumine, offers a still more obstinate resistance: whence it results, that the force of cohesion is not only in opposition to the action of caloric, but also to that of every substance which tends to change the state of a solid body.

We find, therefore, in all bodies, a disposition to become solid, which varies considerably according to their natures; which being always in opposition to the expansive force of heat, is sometimes destroyed by it, because it depends on the distance of the particles; but which is restored, as soon as the expansion, produced by the heat, is diminished to a certain degree.

Under the name of *affinity of aggregation*, some chemists have distinguished the effects of the force of cohesion, from those of the affinity of composition; but they have only admitted it between the moleculæ of the same species, and they have opposed it to the *affinity of composition*, although the force of cohesion may be often one of the causes which produces combinations, and which consequently then becomes that which they call *affinity of composition*.

5. I have observed, that many gaseous substances acquired, by their mutual combination, the property of becoming solid: hence it results that their particles experience, by the act of combination, a change similar to that which liquids undergo by a diminution of temperature, which produces their approximation; or, that the figure of the new molecule is more favourable to their reciprocal action.

It likewise frequently happens that two liquids form, by their combination, a solid substance; from whence it follows, that, in these circumstances, the force of cohesion which could not produce any sensible effect, becomes a preponderating force: this shows, at the same time, an analogy between the effects produced in a substance by a change of temperature, and those which are owing to the combination of two substances.

6. The more the action of caloric on a body is weakened, the greater is the energy acquired by that of the reciprocal affinity, and the nearer are the particles brought together; this is the cause of the diminution in volume produced in bodies by cold: but when a substance passes from a liquid state to a solid state, the force of cohesion itself sometimes produces another effect which is contrary to the first.

7. When bodies pass from a liquid state to a solid state, their particles tend to assume that disposition in which their reciprocal affinity can be exercised.

exercised with the greatest advantage: hence the symmetrical arrangement they take, which constitutes crystallization.

This symmetrical disposition sometimes produces an augmentation of volume, which causes an apparent interruption in the necessary effect of the approximation of the particles arising from the diminution of the action of caloric: so when water congeals, its specific gravity is diminished; and there are metals in which the part which retains its solidity, floats above that which is liquefied; thus, each of them has less specific gravity while solid, than when in the liquid state.

8. Those liquid substances which experience an increase of volume in passing to the solid state, offer a phenomenon which deserves to be noticed. This dilatation of bulk is not only observed at the moment of congelation, but it begins to be manifested in the liquid, when it approaches the point of its congelation,

Mairan was the first who remarked the dilatation of water which approaches the degree of congelation; but it was Deluc who determined the quantity.* He observed that it began to be manifested at about the fourth degree above the point of congelation, and that the diminution, which took place from the eighth degree to the fourth, was only capable of counterbalancing this effect.

He also observed, that the influence of the

* Recherches sur les Modifications de l'Atmosphère, édit. in 8vo. tom. ii.

cause

cause which produces this dilatation shows itself at several degrees above that at which it is manifested by a real increase.

Blagden not only confirmed these observations,* but this experienced philosopher ascertained that the dilatation in bulk continued, even in a greater degree, in proportion as the temperature of the water was cooled below zero, without entering into congelation.

This effect is not limited to the ordinary point of the congelation of water: Blagden observed that when this point was lowered by the dissolution of a salt, the augmentation of volume, which ought to precede congelation, was manifested at nearly the same space of time before it became effective.

9. If it is considered that when liquids approach the point of ebullition, the influence of the elastic state, into which they are about to pass, shows itself, by a greater increase of dilatation, sometime before they are changed into elastic fluids, and that the law of dilatation, to which elastic fluids are subject in a similar manner, experiences, as we shall see, a modification, whenever they approach the point of liquidity, we shall be disposed to admit, as a general principle, that the causes which determine the changes in the constitution of bodies, exercise an action whose effects are sensible even before the change of constitution takes place.

* Philosophical Transactions, 1788.

A first

A first consequence of this principle is, that the reciprocal affinity which can produce the solid state should be considered as a force which acts, not only when the solidity becomes manifest, but before that period; so that in every case in which any solid substance is produced, whether it be by a separation or a combination, the cause itself which produces the solidity must be sought for in the reciprocal action of the parts which acquire that property, although it was not perceived before.

10. All those bodies which pass from a liquid to a solid state do not experience a dilatation occasioned by the arrangement which their parts then assume; there are some, on the contrary, and these are probably the greatest number, which undergo a contraction: thus, nitric acid and sulphuric acid, whose congelation should be very analogous to that of water, experience nevertheless a contraction, which appears even to be considerable in nitric acid.*

Many metals by becoming solid acquire a greater specific gravity, mercury is of this number; and the celebrated Cavendish has explained, by the contraction it suffers, the descent of the thermometer arising from the congelation of the mercury, at the moment in which it operates, and from which temperatures, much lower than those

* An account of experiments made by John M'Nab, by Henry Cavendish. Philos. Trans. 1786.

which

which really takes place, have been believed to be indicated.*

11. It is not only those substances which suffer dilatation in their passage to the solid state, that can preserve their liquidity at a degree of temperature below that of their congelation: Cavendish found that this effect took place in mercury which congealed: he also noticed that it was much more considerable in the congelation of nitric acid than in that of water.

This species of inactivity, which is possessed in common by all the saline solutions when they are at the point of congelation, and which arises either from a difficulty in the change of the position of the molecule, or from that of the passage of caloric from one combination to another, when they are only called into action by a very slight force, is observed in a great number of phenomena, wherein the chemical action has but little energy: this is a subject to which I shall return.

12. Motion given to the particles of water which is below the degree necessary to its congelation, by causing the molecule to pass through a great number of positions, brings together those which are most favourable to reciprocal action; by this means it promotes the congelation: but Blagden has shown that this cause, pointed out by Mairan, had not so much efficacy as was attributed to it; he found that nothing produced this

* Philos. Trans. vol. LXXXIII.

effect more quickly than the contact of a fragment of ice; and the contact of a saline crystal produced an analogous effect in a solution of the same salt: but sand dispersed in water below the point of congelation, did not promote the formation of ice; on the contrary, the earthy parts which remain suspended in the water, and destroy its transparency, fix the congelation to the point at which it would have taken place of itself. These facts show, not only that it is to the force of cohesion, arising from reciprocal affinity, that the solidity, acquired by liquid substances, is owing; but they also prove that the contact of substances, already solid, promotes this effect, whenever they have an affinity with those which should be converted into the solid state, and that, on the contrary, they exert no sensible influence on the phenomenon, if they are destitute of this affinity.

From these observations it may already be concluded, that cohesion which is the effect of the reciprocal affinity of the moleculæ, ought to be considered as a force opposed to that of liquidity; that this force acts, not only while the cohesion exists, but that it is it which renders it effective; and that it exerts itself between the integrant particles resulting from combination, in the same way as between the moleculæ of a simple substance.

CHAR

CHAP. II.

Of Solution.

13. If liquid substances can acquire the solid state by an increase of the force of cohesion, a contrary cause may procure liquidity to a solid body: when this effect is produced by the action of a liquid, it constitutes solution; the union then becomes such, that all the solid which is liquefied is found distributed through the liquid and uniformly blended with it; so that both appear to be one homogeneous substance.

Two liquids of different specific gravities may also, by their reciprocal action, be blended and form but one uniform liquid.

The reciprocal action of two bodies may be so weak as to be unable to counterbalance the resistance of the force of cohesion, or of the distance of their specific gravity, and the effects produced by it should in that case be different, although they are derived from the same cause.

This effect will be found, more or less complete, in all the results of the reciprocal action of liquids and solids; it is therefore a general phenomenon in which the laws of chemical action may be recognized.

The chemical action of different substances is exerted not only in the ratio of their affinity, but also in the ratio of their quantity; one immediate consequence

consequence is, that chemical action diminishes in proportion as saturation advances.

It is by the exact correspondence of the phenomena with the immediate consequences in this principle, and of the circumstances which may be expected to modify its application, that, from a simple supposition, it takes the character of the general law of chemical action; and while the explanations of these phenomena are deduced naturally from it, we ought to reject every other supposition as false and useless: I shall therefore make a first trial of this law of affinity by applying it to the reciprocal action of solids and liquids, and by determining the modifications it should receive from the conditions in which solids and liquids may exert their reciprocal action.

14. A liquid can only exert its action upon a solid by contact with it, or rather within the sphere of activity which its affinity may possess; so that its action on the solid is not increased, whether it is in a large quantity, or whether there may be only as much as is necessary to maintain all the possible points of contact.

Nevertheless, since an equilibrium of saturation takes place through the whole quantity of a liquid, the parts which can act upon the solid, arrive much more slowly at the degree of saturation at which the action ceases; so that the quantity of the solid which is dissolved is proportionate to that of the liquid, in consequence of the general law of affinity.

It

It also follows from this law, that a substance, which is in solution in a quantity of liquid greater than is necessary, is retained therein by a more powerful action, and that, on the contrary, the superfluous quantity of the liquid is subjected more feebly to the affinity of the dissolved substance, than is required for solution: this is conformable to observation,

It will be seen therefore that the general law which I have announced, is, in this instance, only modified by the circumstance which limits the quantity of liquid that can exert its action simultaneously.

15. Chemical action is reciprocal; its operation is the result of a mutual tendency to combination; strictly speaking, it cannot be said that a liquid acts on a solid rather than that a solid acts on a liquid: convenience of expression has permitted the whole of the action to be attributed, without misconception, to one of the substances, when the effect of the action is to be examined instead of the action itself.

This observation may be applied to every property and every phenomenon in chemistry; but the two substances must be examined separately to ascertain the state of the powers they exert on each other, and the changes produced in their properties: let us take, as an example, the action of water and lime.

16. When lime is put into water, these two substances exert a mutual action; but the force of cohesion

cohesion is, at the first, too considerable for the water to effect a solution; it is the lime which begins by imbibing the liquid; in proportion as it is saturated, its force of cohesion is diminished, and when it is sufficiently weakened, the water, which is in contact with it, can dissolve it: two combinations are then established, which exert opposite forces until they have arrived at a state of saturation or equilibrium, in which they are stationary while the conditions remain the same; but if the temperature, or the quantity of water, becomes varied, another equilibrium must take place.

It is the same with all those substances which possess a force of cohesion so considerable that the action of the water cannot overcome it, until it has been sufficiently weakened by the state of saturation which it begins to experience; but if their force of cohesion is slight, or if they are already saturated with water so as to preserve only a very weak cohesion, they can be immediately dissolved in water, and the salts which have retained water during their crystallization are in this state.

If there is not a sufficient quantity of water relatively to that of the lime, only one of the effects mentioned above takes place; the lime will absorb the whole of the water, and communicate to it its state of solidity; nevertheless, the reciprocal action of the moleculeæ of the lime will be so much weakened by the saturation it has experienced,

enced, that it will fall into powder spontaneously.

17. Frequently the water which combines with a solid body cannot weaken its force of cohesion sufficiently to be able to dissolve it; in that case the body is only moistened, without being dissolved in the water: when its affinity for water, weakened by the saturation it experiences, is in equilibrium with the force of cohesion, it ceases to imbibe any more. Frequently also, the action of the water is so weak in comparison with that of cohesion, that it can only adhere to the surface of the solid body and wet it.

18. When the solid is reduced into small masses, or is in a pulverulent state, the action by which the liquid wets these small masses may sometimes hold them suspended in it, and overcome the difference of the specific gravity, without producing solution; it is this which is observed in some chemical precipitations wherein the liquid does not regain its transparency, notwithstanding the difference of the specific gravity between it and the substance which it ceases to hold in solution: so that this suspension announces a reciprocal affinity, which retains the two substances in contact, but which is not sufficient to produce solution.

If the affinity of the liquid for the solid body is still weaker than the reciprocal affinity of its particles, it neither moistens or wets the body: this is the case with mercury, which adheres only to a small number of bodies.

19. The

19. The action of liquids on those bodies which they cannot dissolve is therefore sometimes superior to the mutual action of their peculiar particles, and sometimes it is inferior to it: on this circumstance depends the property possessed by fluids, of raising themselves above the level of their surface, around a solid, placed in them, or of depressing themselves; and by this are explained the properties of capillary tubes, and of the attractions and repulsions observed between bodies floating on the surface of a liquid, which have been thought to be real, but which are only produced by a succession of curves formed by the mutual contact, as has been made appear by Monge in the different cases which show this phenomenon, and of which he has given an explanation as satisfactory as it is elegant.*

20. Two liquids are, in like manner, dissolved when their respective affinity overcomes the force of cohesion and the difference of their specific gravities, which have a tendency to keep them separated; and the characteristics of the solution of a solid will be found in this solution, with this difference, that the resistance to the dissolving power being, in this case, much weaker than that offered by a solid, the solution may more frequently be produced in all proportions, without any difference being perceptible in the superior and inferior parts of the liquid; but sometimes

* Mémoires de l'Academie des Sciences, 1787.

their

their respective affinity is so weak, that, as soon as one liquid is saturated with another, to a certain point, the resistance equals the action; then two combinations are produced, which vary in their quantity according to the proportions of the two liquids: for example, when a little ether is added to a considerable quantity of water, or a little water to the ether, a complete solution is made; but if equal quantities of water and ether are mixed together, two liquids are produced, which remain separate; the upper, which contains a great proportion of ether, and the lower, which contains a great proportion of water: when the quantities of water and ether are changed, other proportions are formed in the two liquids which separate.

Sometimes the reciprocal affinity of two liquids cannot overcome the resistance arising from the mutual affinity of their particles and the difference in their specific gravities: in that case, an effect is produced analogous to that by which a liquid wets a solid; the lightest liquid spreads itself upon the surface of the heaviest, as is the case with oil poured on water: it is this superiority of the reciprocal affinity of the particles of the water over those of the oil which causes a cotton wick impregnated with water to admit none but aqueous particles by suction, or only oily particles if it is impregnated with oil.

There can be no doubt that the moleculæ of a liquid exert a reciprocal affinity, which must be

blended with the force of cohesion, since it terminates in the production of solidity by congelation. It is this which occasions the uniform diffusion of a substance which they can dissolve, and enables them to resist the action of the atmosphere, so as to form drops, and preserve a convexity; but this action may have a certain degree of energy, without the mobility of its parts being destroyed, in the same manner as a metal is malleable; that is to say, they may permit the parts to slide over each other, and still have a great force of cohesion between the same parts. The effect of a difference in specific gravity may also be identified with that of the force of cohesion, but it is generally so small in comparison with the forces which are in action, that it is only in some circumstances that it should be taken into consideration.

21. We have examined the different effects which may result from the opposition of the force of cohesion and the dissolving force, according to their respective intensities: it is obvious that the distinction attempted to be established by some philosophers between chemical affinity and physical adhesion is without foundation; for the effects which they attribute to the latter, depend on the same cause as those which are owing to affinity, and are only different in the energy of the reciprocal action compared with the resistance opposed to it.

22. There is another force which concurs with
the

the action of liquids on solids, and which favours solution, when it does not become an obstruction to it as the principle of elasticity : it is the expansive action of heat, which, when opposed to the force of cohesion, destroys the effect. This cause alone is sufficient to give liquidity to the greater number of solid bodies; but as the dilatation produced by heat in different bodies varies considerably, its effect on solutions is equally variable.

When this cause acts alone, the bodies rendered liquid possess properties analogous to those exhibited by substances held in a liquid state by the action of another substance: nevertheless, it is necessary to separate from the comparative effects, that which depends on the action of the solvent, which I shall examine more particularly in another place.

In the action of two bodies rendered liquid by the sole action of heat, there will also be observed, according to their respective quantities and their dispositions to liquidity, effects, corresponding with those which take place in the action of a liquid on a solid; for example, when tin and copper are exposed to the action of heat, the tin alone is reduced to the liquid state, and dissolves but a small portion of copper, when the temperature is not raised above that which can liquefy the first metal; if the heat is a little greater, it acts more upon the copper, and its action increases as its proportion is more considerable; but if the quantity is very small, its action is confined to the

surface of the copper, which it cannot liquefy : in that case it is only tinned. Two metals sometimes form an alloy in all proportions; sometimes their reciprocal action is too feeble, and they can only combine in the proportions determined by their specific gravities and their fusibility: in this respect they exhibit the properties of solids which are soluble in a liquid, or of liquids which have a weak mutual affinity, and a different specific gravity.

23. Solution is therefore the effect of a power which can overcome the resistance of the force of cohesion, and the difference of the specific gravity. When the resistance is too considerable, it must begin by weakening it, by a commencement of saturation of the substance opposed to it.

When the resistance is sufficiently energetic, it establishes two points of saturation between the contrary forces. These points of saturation are varied by the respective quantities, and by other circumstances which can promote or weaken chemical action.

In the action of a liquid on a solid, the quantities which determine the energy of the action are those included within the sphere of activity; but the quantity of the substance dissolved is proportionate to that of the substance which acts as the solvent.

CHAP. III.

Of the reciprocal Action of the Substances which are held in Solution.

24. WHEN a liquid is saturated with a solid substance which it has dissolved, that is to say, when its action, weakened by the saturation, can no longer overcome the force of cohesion which unites the particles of the solid, the reciprocal action of all the parts actually liquid form one homogeneous substance, which acts in a uniform manner on the rays of light; but, unless the solution is much diluted by a superabundance of the solvent, and consequently the distance introduced between the dissolved particles is carried to a certain point, while the action of the liquid is increased in proportion to its quantity, the force of cohesion must still be regarded as a resistance which continues to act: in fact, it is only necessary to diminish, either the quantity of the solvent, or of the heat whose action assists that of the liquid, to enable the force of cohesion to separate part of the substance dissolved, if the diminution either of the quantity or of the heat is not counterbalanced by an increase of the other: it has been seen that this action discovers itself by sensible effects, before it becomes preponderant, (18).

25. When

25. When, either by the diminution of the quantity of the liquid, or by the reduction of the temperature, the force of cohesion causes a separation of a portion of the dissolved substance, in almost all cases, the parts which are separated form a regular arrangement, which is owing to the relation between their figure and their reciprocal affinity. Hence, those crystals, which nature offers in such variety, and which are produced in so great a number of chemical combinations.

The plates which continue to be added, either because the crystal acts on the dissolved substance, or because the cause of the separation continues to exist in the liquid, are composed of moleculeæ similar to the first, and continue to augment the bulk of the crystal, preserving its first form; nevertheless, this increase may be determined to one face in preference to another, according to the position of the crystal, and the circumstances in which the solution is found.

The crystal, which results from this symmetrical arrangement of the integrant moleculeæ, is so constituted, that by finding successively the joints by which the plates are united, a nucleus is at length obtained which is the same in all the crystals of the same substance; so that all the secondary forms of these crystals arise from the decrement of the plates superadded to the nucleus.

This mechanism of crystallization has been developed

veloped with such superior skill by Haüy, that it has become one of the happiest applications of geometry to the operations of nature; but these results of affinity, and the form of the integrant particles, would lead to considerations detached from chemistry.

26. The substances which are held in solution exert a mutual action which modifies the effects of solution and crystallization; to determine what depends on this action, I shall select those saline substances which are equally remarkable for their solubility, for their crystallization, and for their chemical properties. I shall consider them here but as substances which dissolve and which resume their first state by crystallization, independent of the causes which can change their combinations.

In the first place it must be noticed, that when the solution of a salt is near the point of crystallizing, a crystal of the same salt determines the crystallization: it is thus that, in the common crystallizations, all the saline moleculæ deposit themselves on the crystals first formed; so that all the saline deposition forms a group, if the crystallization is not too much precipitated.

27. The contact of the crystals not only accelerates the separation of that part of the salt which is disposed to be deposited, because it is in greater quantity than the water can hold in solution at a given temperature, but it also causes that of a part which the water could retain, so that this solution

solution is carried beyond the equilibrium of the dissolving force with that of cohesion.

It is not a crystal of the same salt alone which can produce this effect, several bodies operate in the same way, but in a mode less efficacious and unequal to each other; thus, when different solid substances are plunged into the solution of a salt, the latter adheres to some and not to others.

These observations prove that solid substances exert an efficacious action on those which are still liquid, whenever they possess a reciprocal affinity which has a slight energy, and what has been said on the congelation produced by the contact of ice also confirms it, as well as the properties of capillary tubes.

28. In the solutions which are produced by a weak chemical action, the specific gravity of the substance dissolved occasions a sensible effect, either in the proportion of the substance dissolved which is greater in the lower part of the liquid than in the upper, or in the deposition of the saline parts which unite with those already solid, and in this last effect it concurs with the action of the solid. On this occasion I shall quote an interesting observation of Leblanc.

He says,* " Into a vessel about two inches in diameter and two feet high, I put a solution sufficiently concentrated to crystallize: I suspended crystals of the same species in the li-

* Journal de Phys. tom XXXIII, p. 376.

" quor,

" quor, at different heights almost to the surface:
" I repeated this experiment on different salts,
" and obtained the following results: when the
" liquor was sufficiently concentrated all the
" crystals increased, with this difference, that
" the increase was greater in proportion as the
" crystal was near the bottom of the vessel; and
" as the liquor, by rest, became deprived of the
" saline moleculæ, the crystals decreased by gra-
" dations similar to those of their increase. At
" length the crystals which were nearest to the
" surface were totally dissolved, while those
" which were at the bottom obtained a further
" increase; and these last continued to grow
" larger on the side which touched the bottom of
" the vessel, while the opposite side of the same
" crystal was, in its turn, dissolved by the effect
" of the reciprocal action of the parts in solu-
" tion."

29. A saline solution may be brought, during evaporation, to a point of saturation much greater than it could have attained by solution with the same quantity of water, and at the same temperature: what I have said on water which can undergo a degree of cold greater than that which is necessary for its congelation (8), may be applied to this super-saturated solution. Motion communicated to it, produces also a sudden crystallization by disposing the saline parts in the liquid in such a manner that their reciprocal affinity can be exerted with more advantage; but this effect would

would only be instantaneous, if the first crystals did not afterwards act on the moleculæ which remain in solution. (26).

This mutual action of solids, which tends to give their constitution to substances held in solution, and with which they exercise a reciprocal affinity, as well as that of liquids which, on the contrary, tends to produce liquidity by destroying cohesion, and the successive effects of these two powers, which may, each in their turn, become superior, from a change of circumstances, deserve great attention in the explanation of natural phenomena.

30. The mutual action produces also other effects which must be noticed; experience shows that when water has dissolved a salt to saturation, it can still dissolve another species, and, by that, it even regains the faculty of dissolving a new quantity of the first salt;* if the dissolving power of the water was not seconded by another cause, since it diminishes on account of the action it exercises, it could not act on a new substance without abandoning that which has engaged its dissolving power, it follows therefore that one salt must act on the other, and that their mutual action diminishes the resistance of their force of cohesion, and by that means assists the action of the water.

31. When the action of the solvent is weakened,

* Vauquelin, Ann. de Chim. tom XIII,

either

either by diminishing its quantity, or by lowering its temperature, the substance which was held in solution is separated, because of its insolubility in these new circumstances; but if there are several salts which act on each other, their solubility is augmented unequally not only in the ratio of their mutual affinities, but also in the ratio of the proportions in which they are found: hence it arises, that when a liquid contains several salts, they are separated with difficulty by a first crystallization, unless they differ greatly in their force of cohesion: but by repeating the crystallizations after the first separation, the quantity of one salt which is blended with another becomes more and more diminished; it no longer retains a resistance to the action of the solvent sufficiently strong to oppose the separation of a salt which has a greater force of crystallization, and it sometimes terminates by a complete separation; but sometimes the two salts are mingled together, particularly if there is no great difference in their solubility, and, in crystallizing, they assume a particular form, or preserve that which is peculiar to one of the two. It is in this manner that sulphate of iron and sulphate of copper unite and compose a complex salt, although the solubility of the first is greater than that of the second;* and that, in the gypsiferous muriated soda,† the sulphate of

* Leblanc, Journ. de Phys. tom XXXI.

† Haüy, Traité de Minér. tom II. p. 365.

lime takes the form of the muriate of soda, notwithstanding it is more abundant in the combination than that salt; finally, after the separation of the crystals, the liquid often retains an incrystallizable residuum, to which the name of mother-water is given, and which arises either wholly or in part from the mutual action of the saline substances.

If the force of crystallization of two salts is not considerable, the mutual action they exercise may overcome it, by which means they lose the property of crystallizing, and the relative power of the water is increased, or only part of the two salts is obtained, according to the proportions which have been put into the solution: the rest remains blended in the liquid state, and cannot be made to crystallize by simple evaporation and rest.

32. There are even salts which have so little force of cohesion, that the action of water, however small the quantity, is sufficient to prevent their crystallization; in that case the force of cohesion may be considered as null: the affinity of these substances for water also seems to be strong, because its whole effect is exerted: salts of this description easily attract humidity, and are said to deliquesce; but notwithstanding they are deliquescent, the facility with which they take the crystalline form by means of alcohol, which diminishes the action exerted on them by the water, proves that they possess an active cohesion.

For

For the same reason, these salts act with energy on others, so that if they do not meet with a considerable resistance from their force of crystallization, they retain a greater or less proportion in the incrustallizable residue.

33. If it is wished to ascertain this effect of deliquescent salts, the substances which remain in the incrustallizable liquid must be examined : if a deliquescent salt, in a state of desiccation, is added to a saturated solution of a crystallizable salt, it may lead to an erroneous conclusion, because the action will be compound : the deliquescent salt will have a tendency to attract the water, at the same time that it acts upon the other salt, the effect will therefore be also compound : on the one hand, the saturation of the water will tend to produce a precipitation ; on the other, the action of the deliquescent salt will augment the solubility of that which is capable of crystallization.

34. We have seen (16), that when a solid is dissolved in water, two combinations may take place ; in one the solid substance retains part of the water ; in the other, the liquid holds in solution part of the solid : these two compounds correspond to the dissolving force, and to the force of cohesion, so that if the quantity of the liquid be too small, it will be entirely absorbed, as the solid will wholly disappear if its quantity be too small : in each variation of these relations, proportions corresponding to the two combinations are established, besides the two extremes, that is to

to say; 1st. the point at which all the solid can be held in solution by the liquid; 2d. that in which all the liquid can be reduced to the solid state.

When the quantity of the liquid is diminished by evaporation, or when its dissolving power is weakened by a reduction of temperature, a part of the salt separates and crystallizes; the liquid which remains in a state of saturation opposes but a feeble action to that by which the separating solid tends to retain a portion of water, which promotes, but which also modifies, the symmetrical arrangement of its parts.

This water interposed between the saline particles loses its liquidity by the action it experiences, but cannot in this state be strictly compared with ice, in which the reciprocal affinity has produced an arrangement which has increased its volume: it serves, by its intermediate action, to unite into large crystals, the moleculæ, which by the sole action of their reciprocal affinity could only form into much smaller detached masses; so that by driving off this water in any way, the form of the crystal is destroyed, and the saline substance is reduced into much smaller masses, whose mutual affinity is no longer capable of producing any effect, until their force of cohesion has been again overcome by water or by heat.

35. This intermediate water is not necessary to all crystallizations, for there are many crystals, particularly among substances of little solubility, which

which appear not to admit it, or to have but a very small quantity. There are some which seem to be capable of crystallizing either by retaining a certain portion of water of crystallization, or without the assistance of this water; but this circumstance is sufficient to change the form of their crystals; for it is probable, that from this cause arises the difference in the forms of the crystals of the anhydrous sulphated lime and sulphate of lime,* and, as Haüy conjectures, in those of the arragonite and the other carbonates of lime.

It appears that salts possessed of a considerable force of cohesion retain much less water than those which have but a feeble cohesion; in fact, the reciprocal affinity of the saline moleculæ must be an obstacle to their action on water; hence it follows, that salts may retain a quantity, and nevertheless exercise a weak action on it, as is observed in several salts which are naturally efflorescent, that is to say, which easily yield their water of crystallization to the air. A more powerful action on this liquid, added to a weak cohesion, gives them the property of being deliquescent.

This water, which is only retained by a weak action, contributes to but few of the properties of the saline substances whose elements exert a much more powerful reciprocal action; it is rather a medium which causes a variation in the pheno-

* *Traité de Minér.* tom IV. p. 348.

mena arising from the force of cohesion, than a part of the substance; but this medium has much influence on the phenomena of the crystallization, which must be distinguished from those arising from the action which the substances are capable of exerting on others by their distinctive affinity. It is from this cause that the circumstances of the crystallization may occasion many changes in the form of the crystals, although they have no influence on the properties of the substance, and there will probably be found but little analogy between the form taken by a substance which has been liquified by heat, and permitted to cool gradually, so as to enable its moleculæ to assume a symmetrical arrangement, and that which it would take in crystallizing by means of water.

Those causes which favour the liquidity of substances diminish the effect of the force of cohesion, even when they have attained the solid state. Hence it arises, that the salts which retain much water in the composition of their crystals are easily liquefied by heat; this liquefaction, which is denominated aqueous, is distinguished from that produced by the action of heat alone: the first liquefaction does not take place in salts possessed of a considerable force of cohesion, or which have retained but little water during their crystallization.

The reciprocal action of two substances produces therefore effects similar to those of the action which the moleculæ of each mutually exert.

exert. They are modified by each other in their relation with the force which produces solution.

CHAP. IV.

Of Combination.

36. IN the preceding chapters I have considered those effects of reciprocal affinity which produce the cohesion of the moleculæ, and afterwards those which arise from the opposite action of the force of cohesion, and of a liquid which tends to destroy it; but all chemical action between two substances of different natures produces an effect analogous to that which arises from the mutual affinity of similar moleculæ; it forms, or tends to form a union between them, which is the product of their mutual affinity, and which varies according to the force of that action, and according to the resistance opposed to it. It is to this union of two substances, as well as to the act which has produced it, that the name of combination is given.

From this it results, that solution is a true combination, and that its weakest action is owing to the same cause: the only difference there is between them relates to the form under which they are considered; in solution, the attention is principally directed to the liquidity which a solid

body acquires by the combination, and particularly to the uniformity of the parts of the compound liquid: the same idea is applied to gaseous solution. In combination, the other properties of the compound which is formed, and which result from the union of its elements, are principally considered, and compared with those possessed by the substances which are united: in most cases, solution is only owing to a feeble combination which has not caused the characteristic properties of the dissolved body to disappear.

One consequence of the preceding observations is, that we must follow the same laws in combination as have been observed in the chemical action which produces dissolution.

Since all reciprocal action produces a combination, all the chemical properties which distinguish a substance are derived from its affinities, or its tendency to combine with other substances, and all the phenomena to which it contributes depend on the combinations into which it enters, or from which it is eliminated; so that combination, which is the result of all chemical action, is the general cause of the chemical effects produced, or of the phenomena, the explanation of which is attained by comparing them together to discover their mutual dependence, and by considering them under each relation with every combination which they produce.

37. Among the affinities of a substance there is frequently one which predominates, and which stamps

stamps it with a peculiar character, and, upon which the principal part of its properties are dependent. It is these predominating affinities which are more particularly serviceable in the classification of the chemical properties of different substances, and of the chemical phenomena derived from them: thus, affinity for oxygen distinguishes inflammable substances; the reciprocal affinity of acids and alkalis constitute acidity and alkalinity; for this reason, these affinities and their effects are the principal object of chemical consideration.

Characteristic affinity supposes properties in the two subjects of the combination (and what I assert of two, must be applied to all those which enter into a complex combination), which render them opponents; so that one cannot predominate but at the expense of the other, and an equality of force produces a state in which neither the character of the one nor of the other can be perceived; this is the state which is called neuter, and which is not found in the reciprocal action of acids and alkalis alone, but also in that of all the opposing powers.

38. On considering that which is observable in the mutual combination of two adverse substances, as, for example, of an acid and an alkali, it will be found that the acidity diminishes in proportion to the increase of the alkali, and that a degree of saturation will take place, at which the properties of both acid and alkali equally disappear and be-

come latent; nevertheless, by a continued addition of the alkali, its character will re-appear, and become more and more predominant.

It will be obvious then, 1st. that acidity and alkalinity mutually saturate each other, and may become alternately predominant, according to the proportion in which the combination is effected: there is no obstacle, no suspension of the progress of the combination and of the saturation which accompanies it, unless the force of cohesion or of elasticity produces a separation, in which the proportions are determined by one of these two conditions.

2d. That the acid and alkaline properties diminish according to the degree of saturation experienced by the acid and the alkali; so that the same characters are found in a chemical action of the greatest energy which we have noticed in the weakest degree produced by solution, (14).

39. Some chemists, influenced by having found determinate proportions in several combinations, have frequently considered it as a general law that combinations should be formed in invariable proportions; so that, according to them, when a neutral salt acquires an excess of acid or alkali, the homogeneous substance resulting from it is a solution of the neutral salt in a portion of the free acid or alkali.

This is an hypothesis which has no foundation but a distinction between solution and combination, and in which the properties which cause a separation

separation are confounded with the affinity which produces the combination; but those circumstances must not be overlooked which can determine the separation of combinations in a certain state, and which, by that means, limit the effects of the general law of affinity.

It is not always at the point of neutralization that a separation takes place: the acidulous tartrite of pot-ash separates and crystallizes more easily than the neutral tartrite: will it be asserted, that the latter is held in solution by the excess of acid? For the present, I believe I may confine myself to this instance.

40. From what has been shown it is necessary to distinguish two species of saturation; one is the extreme of the chemical action exercised by one substance on another, in given circumstances; for example, water is said to be saturated with a salt when it cannot dissolve any more, although neither the properties of the water nor the properties of the salt have experienced saturation: the other is the point at which the adverse properties of one substance are hidden by those of another, and are in that equilibrium which produces the state of inaction called neutralization: this second saturation is seldom met with at the same time as the first.

When a combination is formed, its two elements are retained in it in the ratio of their mutual affinity and of their respective quantity; so that, in conformity to the general law of chemical action,

if

if one of the two predominates, that part which is in excess is held with the less force by its opposing substance in proportion as its excess is greater; but, as in the neutral state, the action of each element on its opponent is far from being exhausted, we see how a neutral salt may be subjected to the dissolving action of water, without producing any change in the state of its combination; nevertheless, when there is a material difference in the action exercised by water on each of the two elements, and when the action which unites them is not very energetic, that of the water is capable of producing considerable variations in the combination, as I shall notice more particularly in treating of the action of solvents.

41. The force of cohesion offers a resistance to the energetic action which produces combinations, in the same way as it does in solutions; hence it must not be concluded, because a combination does not take place, that the two substances have no mutual affinity: alumine, however divided, cannot be dissolved directly by the acetic acid; but if a solution of sulphate of alumine is mixed with a solution of a salt containing acetic acid, this combination can be formed and maintained; there could only be the force of cohesion which united the moleculæ of the alumine, to oppose the combination in the first case. All the acids can hold silex in solution, if it has been previously dissolved by an alkali; but if the moleculæ of the silex are consolidated by desiccation, the force of cohesion

cohesion which keeps them together opposes their solution in the acids, with the exception of the fluoric acid.

42. It follows from what has been said above, that the most powerful, as well as the weakest, chemical action is exerted in the ratio of the reciprocal affinity of the substances and of the quantities within the sphere of activity; that the action diminishes in proportion to the saturation, and that there is no point at which it determines the proportions, but that the limits of these proportions, in the combinations which it forms, and those of its power, are to be sought for in the forces which are opposed to it: finally, two effects of chemical action must be distinguished, that by which it produces a reciprocal saturation, and that which causes a change in the constitution.

43. When two substances exercise a chemical action, the properties dependent on the affinity which unites them, and which is in reality no other than their mutual tendency to combination, in the different circumstances in which they may be found, experience a saturation proportionate to their mutual action: they become latent, and do not re-appear in either of the substances, unless its action becomes predominant over that of the other, or it becomes free.

On the other hand, the properties which depend on the constitution experience only those changes which have a relation with the constitution itself, which

which sometimes is the mean of that of the two substances which combine; while, in other circumstances, one of the two substances communicates its state to the other, but with modifications which depend on the new union. In this effect there is no saturation; nothing can be perceived but the reciprocal action of the moleculæ, which, according to the force of their mutual affinity, and, according to the relation they have with calorific, experience a condensation more or less considerable, and acquire a greater or less disposition for solidity, liquidity, or elasticity: the effects produced by this reciprocal action are very analogous to mechanical effects.

In this way the same cause produces two series of properties which must be considered as particular forces concurring in the chemical phenomena, or producing effects which counterbalance or destroy each other.

One of these two forces may be so superior to the other, that the action of the one cannot begin until the other is weakened: thus, in condensed clay none of the properties which characterise it can be found, until the force of cohesion which unites its moleculæ has been destroyed.

Besides these predominating affinities, which are the basis of the characteristic properties of substances remarkable for the energy of their action, there are also secondary ones, which give other properties to them, and which also follow the same

same laws of saturation; but their effects disappear whenever the superior affinity is called into action.

In the relation of the acids with the alkalis we shall examine more particularly the mutual action of the substances which combine, and whose properties are reciprocally saturated by each other.

SECTION

SECTION II.

Of Acidity and Alkalinity.

CHAP. I.

Of the reciprocal Action of Acids and of Alkalies.

44. AMONG those substances which are endowed with a strong reciprocal affinity, the acids and alkalis deserve to be distinguished by the energy of their action, by the number of combinations they form, and by the influence they possess in the phenomena of nature, and in the operations of the arts; on which account they furnish the greatest part of the materials which have served to establish the principles of the science, and for this reason I shall dwell particularly on the examination of their chemical action.

The acids and alkalis may be considered under different views; for example, under that of their composition, of the modifications they may experience by a change of constitution, and of the differences which, in this respect, distinguish them from each other; or under that of the reciprocal action they exert as acids and as alkalis. In this place I shall only attend to the reciprocal exercise

exercise of one general property of acids and alkalis, of acidity, and of alkalinity.'

45. There are substances which act like acids with alkaline bases, and like alkalis with the acids; such are the greater part of the metallic oxides: they may be assimilated with acids when they perform their functions, and with alkalis when they combine with the acids; nevertheless, this resemblance is imperfect and useless in the classification of their properties. There are other substances in which the acid or alkaline properties are so weak that they do not afford a predominating character; the peculiar properties of these substances must be examined: but all that belongs to the chemical action of acids and alkalis will be found in every chemical action which, by its energy, produces a saturation of the distinctive properties.

46. The distinguishing character of acids is to form combinations, by their union with alkalis, in which the properties of acidity and alkalinity can no longer be discovered, when the proportions of the acid and the alkali are such as to produce that degree of saturation called neutralization.

Acidity and alkalinity are therefore two comparative terms of one species of combination; but, like other bodies, acids and alkalis possess properties which depend on the reciprocal action of their molecules, and which may modify the effect of their mutual tendency to combination: these properties cannot experience saturation; but they increase

increase or diminish according to the state of the combined moleculæ, which then supply the place of the simple moleculæ of the uncombined acid and alkali.

It is necessary therefore carefully to distinguish the effects of saturation from those which result from the reciprocal action of the integrant particles of the combination, as well as to distinguish, in an acid or an alkali, their reciprocal tendency to combination from the effects of their volatility, of their fixity, of their cohesion, or of their specific gravity.

Besides its affinity for the alkalis, an acid has secondary affinities which cause some differences between it and the others; but that which it has for the alkalis exerts the most powerful action, and produces its principal properties; when that can act, it destroys all the combinations that might have been formed in consequence of the other affinities; so that it is to be considered as a predominating affinity which characterises it.

47. Hence it follows, that, in the comparison of the acids, the first object which will fix the attention, is the power with which they can exercise the acidity which forms their distinguishing character; now this power is estimated by the quantity of each of the acids which is required to produce the same effect; that is to say, to saturate a given quantity of the same alkali. It is therefore the capacity for saturation of each acid which, in ascertaining its acidity, gives the comparative

parative force of the affinity to which it is owing; but the properties of each combination must be derived from those of its elements, which are simply modified by the act of combination.

In fact, all the acids produce a similar result, and exert an equal force in neutralizing the alkalis, but it will be seen that they do not all possess the same power if a comparison is made of their quantities; a greater or less proportion of each is required to produce the same effect; it is in this that the difference of the energy of their affinities consists.

It may therefore be said, that the affinity of the different acids for an alkaline base, is in the inverse ratio of the ponderable quantity of each of them which is necessary to neutralize an equal quantity of the same alkaline base; but by proportioning the quantities to the affinity, they produce the same effect; so that the force put in action depends on the affinity and on the quantity, and one can supply the place of the other.

48. I have designated by the name of *chemical mass* this faculty of producing a saturation, this power, which is compounded of the ponderable quantity of an acid and of its affinity: according to this definition, the masses which are put in action are proportionate to the saturation they can produce in the substance with which they combine.

An acid is therefore the more powerful, when an equal weight can saturate a greater quantity of an alkali;

alkali; the same comparison of power may be observed between the acids, when their action is required to overcome the force of cohesion ; and that which has been stated on the reciprocal action of a liquid and a solid, with the modifications which follow, must be applied to them.

49. In the first place, the power of an acid, which is estimated by its capacity for saturation, must be distinguished from the energy which depends on its concentration : a homogeneous liquid, such as water, has always the same solvent force, at an equal degree of temperature; but an acid may be diluted in a greater or less quantity of water, and by that means, the quantity within the sphere of activity may be so weakened, as to be insufficient to overcome the force of cohesion, which the same acid, in a greater state of concentration, could have accomplished; it is generally in this sense that an acid is said to be strong or weak.

In the second place, the combination of an acid with a base, acquires a force of cohesion more or less considerable. This force of cohesion, which arises during a combination, is generally the strongest at the point of neutralization; but sometimes it takes place at another degree of saturation.

50. It follows from the preceding observations, 1st. That all those substances which can saturate the alkalis, and cause their properties to disappear, ought to be classed among the acids; in like manner,

ner, among the alkalis should be placed all those which by their union can saturate acidity.

2d. That the capacity for saturation being the measure of this property, it should be employed to form a scale of the comparative power of acids, as well as of that of alkalis.

In the combination of the acids with the alkalis, the affinity shows very distinctly the two effects of saturation, and of the mutual action to which the force of cohesion is owing: by the first, the opposing qualities are rendered imperceptible; by the second, the properties which depend on the distance of the molecule are, on the contrary, strengthened; for the force of cohesion is more powerful in saline combinations than it was in their elements.

51. In neutral combinations therefore, the characteristic properties of their elements are no longer perceptible; but those which belong to these combinations, while they exist in their integrity, are almost wholly derived from the reciprocal affinity of the integrant parts of the compound: such are the fusibility, the volatility, the fixity, the hardness, the attributes of crystallization, the specific gravity; but as the properties of combinations, which depend on the reciprocal affinity of the integrant parts of the compound, bear a constant relation to the properties of the elementary parts, I shall endeavour in the sequel, to ascertain what this relation is, and what are the conditions which cause it to vary.

In

In the succeeding chapters I shall employ the force of cohesion, which belongs to combinations or even to their elements, to explain the effects dependent on it, which have been confounded with those of the affinity produced by saturation; but I shall confine myself to the consideration of this force, as the cause of the separations which take place independently of those circumstances which produce a very powerful effect in a certain degree of saturation.

The principles laid down in this chapter may be proved, by examining whether they correspond exactly with the phenomena produced by the reciprocal action of acids and alkalis in the different circumstances in which it is exercised.

CHAP. II.

Of the Action of an Acid on a Neutral Combination.

52. WE have seen that all the acids have the property of saturating the alkalis, and of forming neutral combinations, but that different quantities are required to produce this effect; so that each acid, at an equal weight, has a capacity of saturation for each species of alkali, which is peculiar to it.

When a neutral salt is dissolved and an acid is added.

added to the solution, or when the solution is made by the means of an acid, this enters into a competition with the combined acid; they both act on the alkaline base, in the ratio of their respective masses, as though no combination had existed. Each acquires the same degree of saturation, so that the common saturation is equal to that which would have been obtained, if a quantity of a single acid had been employed, which, in its capacity for saturation would have been equal to the two put in action.

It cannot therefore be said, if all the circumstances remain equal, that one acid displaces another from the base with which it had been united; but it shares the action which had been exercised on the base to produce saturation, in the ratio of the masses employed: the first which was in combination, loses as much of its union with the base as the second acquires, and by this loss it recovers its power to act on other substances, by means of the acidity it preserves.

53. These are the consequences which are immediately derived from the properties of affinity, but a different theory has been formed; the affinity of an acid for a base has been considered as *elective*, that is to say, a property has been attributed to it of entirely withdrawing the acid of a combination and of supplying its place, and on this comparative power, tables of affinity have been constructed.

Nevertheless if it is considered that an acid
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exercises a powerful action on a neutral combination ; that with a very few exceptions, it dissolves all the neutral combinations, notwithstanding the resistance of their cohesion, and that its action is more powerful as it is more concentrated, it must be acknowledged that it does exercise its chemical action on the combination, and, that consequently this action must be proportionate to its affinity, or its capacity for saturation and to its quantity. Even water exercises its chemical action ; it is by this force alone that it produces the solution of a neutral combination, and if it does not change its state of saturation, it is only because all its action is not equivalent to the mutual tendency retained by the two elements of the combination ; but when this is only the consequence of a weak affinity, water is able to produce another state of saturation.

I have shown by direct experiments,* that the combinations which were considered as produced by the elective affinities, to which the greatest superiority had been attributed, yielded to others which were thought to be inferior, provided the circumstances which tended to maintain the first were weakened.

54. The effects which were owing to the force of cohesion, or to the elasticity which produced the separations of the combinations, have therefore been confounded with the mutual affinity by

* Recherches sur les lois de L'Affin. Mem. de L'Instit. tom. iii.
which

which their acid and alkaline properties were saturated and brought to a neutral state.

In the action of an acid on a neutral combination, let us consider the effects of the force of cohesion which results from the reciprocal action of the elements of this combination, whether it exists before the intervention of an acid, or whether it becomes a consequence of it.

55. The disposition to solidity which belongs to determinate proportions of an acid and an alkali, and the insolubility arising from it, are sometimes so great, that the combination is formed and wholly separated, although there may be a great excess of acid; thus, when a solution of barites is mixed with sulphuric acid, all the barites separates and is precipitated in a sulphate; the action exercised by the liquid on the combination which is forming, cannot overcome the resistance offered by its insolubility, and this effect is independent of the difference of acids, because sulphuric acid itself has no further action on this precipitate, unless it be in a state of concentration to which the other acids cannot be brought.

But if the insolubility is not also considerable, it may be overcome by an excess of acid, greater or less according to the degree of its insolubility; thus, oxalic acid precipitates, in oxalate of lime, only a part of the lime which forms a neutral salt with another acid: as soon as the acid of the combination has acquired a certain energy by the diminution of the base, it counterbalances the tendency

dency to insolubility, and the oxalate of lime ceases to be separated: the insolubility of phosphate, or sulphate of lime, is still more easily overcome; a weak acidity is sufficient to cause that effect to disappear.

56. When, therefore, two acids act on an alkali, an equilibrium of saturation takes place, which is the product of the quantity and of the relative capacity for saturation of each of the two acids; but when a combination is formed which precipitates, two compounds are produced which exercise opposite forces (16); one is formed by the insoluble combination, and the other is the combination which remains liquid, and which has an excess of acid; this exhausts its solvent action on the insoluble substance; the results depend on the insolubility compared with the energy of the acid; but as the action of acids is proportionate to their quantity, by augmenting the quantity of the acid opposed to the insolubility, that of the precipitate may be diminished, or it may be made to disappear, unless the force of cohesion be too great to yield to that which tends to destroy it.

57. When a separation takes place, whether by an immediate precipitation, or by crystallization, the liquid which remains, except in the few cases in which the opposed acid is wholly separated by forming an insoluble combination, is composed of a part of the two acids and a part of the base: it must not be considered as a solution of the insoluble combination by the other acid; both the

acids exercise their powers on the base, both act in the ratio of their energy and of their quantity, and acquire an equilibrium of saturation (52).

58. The uncrySTALLizable residues, in which (31) only the reciprocal action of the neutral substances have been attended to, may be much increased by an excess of one of the saturating substances; the method of bringing them to the conditions mentioned is, to take away the excess of the acid or alkali which opposes the crystallization.

Sometimes the substance separated by the force of cohesion, is not a simple combination of one of the acids with the alkaline base, but is formed of certain proportions of the two acids and of the alkaline base, which are endowed with an insolubility that causes their separation, in the same manner as in a simple combination, and for the same reason.

59. We have seen what happens when two acids concur in their action on a base in a liquid; but the results are varied in some circumstances when an acid exerts its action on an insoluble combination already formed, because the force of cohesion may be very different in the same species of combination, as we have seen that it might vary with respect to solution, and what has been said on that subject may be applied to this.

The acid, therefore, does not, in that case, act in the ratio of its total quantity, but in the ratio of the quantity within the sphere of activity in which its energy is opposed to the resistance of the cohesion

cohesion.(14—19) Its action becomes weaker as it approaches the state of saturation ; that of the solid combination, on the contrary, remains the same, because it is only on the surface that it can be successively exercised ; so that a degree of saturation shortly takes place in the liquid, at which the resistance can no longer be overcome : hence the utility of all the processes which are employed, either to multiply the points of contact, or to diminish the force of cohesion of the solid parts, and hence the difference observed between a recent combination in a divided state, and the same combination which has been dried or urged by a strong fire.

60. The action of an acid or an alkali on a combination, which, in a liquid state, is exerted in the ratio of the mass, is therefore modified when the combination is solid, or when that which it forms becomes so: hence the effect of the cohesion which belongs to it, and the result, vary, according to the state of this force, and according to the quantity and energy of the acid and alkali within the sphere of activity.

The preceding observations may be applied to the action of an alkaline base on a neutral combination ; but the force of cohesion, which is much more considerable in some of these bases than in the acids, has, from that cause, a more considerable influence on this action.

If a mixture of equal parts of soda and sulphate of pot-ash, is brought to a state of desiccation, and

and afterwards the excess of the alkali is carried off by the action of alcohol, the residue will be composed of sulphate of pot-ash and sulphate of soda.

The sulphate of pot-ash being much less soluble than the sulphate of soda, will separate first; if the mixture is evaporated without separating the excess of the alkali, it will, from that circumstance, seize the greatest part of the acid, and there will remain only an uncrystallizable residue with excess of soda, in which part of the sulphate of pot-ash will be retained.

61. Since alcohol dissolves pot-ash and soda equally, its action causes no sensible change in the result of the reciprocal action of the acid and the two alkalis: this experiment, therefore, is calculated to show the participation of the action of an acid on two alkalis, independently of the effects of the force of cohesion of the two combinations: but if muriate of soda is treated with lime, there will be scarcely any traces of the decomposition of the former, because the lime, having but little solubility, can only act in a very small proportion, and as the evaporation advances its insolubility tends to separate it, while all the mass of the soda is opposed to it: in this case alcohol is not capable of showing the action, because it cannot separate the alkaline base.

The action of an acid or of an alkali on a combination, which, in a liquid state, is exerted in the ratio of the mass, is therefore equally modified when

when the combination is solid, or when that which it forms becomes so : hence the effect of the cohesion which belongs to it, and the result, vary, according to the state of this force, and according to the quantity and energy of the acid and alkali within the sphere of activity : from hence proceed the precipitates whose conditions will be next considered.

CHAP. III.

Of the Precipitates produced by Acids or by Alkalies.

62. WHEN an acid forms a precipitate, by its combination with an alkaline base which it separates from another acid, the insolubility which causes the precipitation, belongs to the natural qualities of each of the elements of the combination, the tendency of which to become solid is increased by the condensation they experience.

The insolubility which derives its origin from this cause determines the proportions of the elements of the combination precipitated, it only yields, more or less, to the acid remaining in the liquid ; so that the operation of the superabundant acid is confined to the diminution of the quantity of the insoluble combination ; but when an alkaline base produces a precipitation, its effect

effect may be different according to the properties of the precipitated base, because the alkalis are very different from each other, in respect of solubility.

63. If this base is soluble by itself, if it is the combination it forms which becomes insoluble, it is in the same situation as the preceding: the combination which separates must also have determinate proportions; an excess of alkali renders the precipitate more soluble and diminishes the quantity, or dissolves the whole of it.

But if the base, insoluble by itself, requires a certain portion of the acid to become liquid, then another alkaline base, by abstracting part of the acid, deprives it of its solubility: it will precipitate by forming an insoluble combination, which may vary in the proportions of its elements.

An alkali which acts on a solution of a salt with an earthy base, shares, therefore, its action on the acid with this base, but the latter requires all the effect of the acid with which it was combined to preserve its solubility, such as it was; in proportion, therefore, as the action of the acid on it diminishes, insolubility takes place, and increases until the separation is accomplished; the acid is divided between the alkali and the earthy base, in the ratio of the forces which are in action at the moment of the separation, so that two combinations are formed, the one soluble and the other insoluble.

Thus, when by means of an alkali, the alumine and

and magnesia have been precipitated from the soluble combination they formed with sulphuric acid, it is only necessary to dissolve these precipitates again in an acid, such as the muriatic, or nitric acid, and then add a solution of barites to obtain a considerable quantity of sulphate of barites, which proves that the sulphuric acid was combined with them. The metallic solutions, and particularly those of mercury, afford proofs, equally convincing, that the precipitates retain part of the acid.

64. It is not, however, to be concluded from this, that precipitates can never be reduced to a simple state: the increase of the force of cohesion in a substance in which it is powerful, is even sufficient, in some cases, to separate an acid from it, with which it has in other respects but a weak affinity; for example, it is enough that silex, dissolved in any acid but the fluoric, should be exposed to a strong desiccation, to cause it to quit the acid and become insoluble: we shall also see that the force of cohesion of some metals can determine their precipitation in the metallic state, without retaining any of the acid which held them in solution; but it appears that this complete separation never occurs between the acids and the alkalis: the quantity of the acid alone may be diminished more or less, according to the force of the alkali which tends to abstract it from a precipitate, whose insolubility does not depend on determined proportions.

If

If the quantity of liquid employed as a solvent is sufficient to counterbalance the insolubility produced by the diminution in the action of the acid, no separation takes place, and then each base acts upon the acid in the ratio of its mass; thus Bergman observed,* that pot-ash or soda did not disturb the transparency of a salt with base of lime when the salt was dissolved in fifty times its quantity of water; if the acid did not continue to act on the lime, the precipitate would have appeared in a much greater quantity of water, for it requires nearly seven hundred parts of water to dissolve one of lime.

If ammonia does not produce a precipitate, like a fixed alkali, with calcareous salts, it is because it has the property of combining with them and forming a triple salt, which is not separated by evaporation, unless the action of the liquid is weaker than its insolubility.

65. Two species of precipitates may therefore be distinguished; those in which the acid and the base acquire, by combination, an insolubility, not possessed by either in an insulated state, or which they had in a much less degree; such are the various salts which form precipitates if the water is not sufficient to hold them in solution, or which crystallize when that is lessened in which they were dissolved; and those precipitates whose base has only acquired solubility by the action of the

* De Attract. Elect. § vii.

acid,

acid, and which form an insoluble combination whenever that action is diminished. The precipitates of the first species have limited proportions in the elements of their combination, or at least these proportions are liable to very slight variations, as I shall notice in another place. Those of the second may be composed of very variable proportions, until the quantity of the acid is such that the increasing action of the base will not allow of its being further diminished; for they can, in precipitation, retain different proportions of the acid according to the state of the forces in action. A proof of this is, that after having formed an insoluble salt with an earthy base, even though it shows a strong affinity, and though a great force of cohesion has caused its precipitation, such, for instance, as sulphate of barites, a portion of its acid may be abstracted by the action of a concentrated alkali. A still greater effect may be obtained by treating phosphate of lime in the same way.

It is therefore very probable, that in these cases the precipitates are different according to the circumstances of the operation; according to the energy of the alkali which produced them, and, consequently, according to its degree of concentration; but as the circumstances vary at the commencement and at the end of the precipitation, when the mixture of the liquids is not made suddenly, the action of the alkali being much stronger at the beginning, than as the saturation advances,

advances, it is very probable that the precipitate varies in the same manner; this is particularly observable in metallic precipitations.

These variations not only accord with those of the circumstances of the operation, but they are also different according to the reciprocal affinity of the elements of the combination which forms a precipitate, and according to the force of cohesion peculiar to them, as we have seen with respect to sulphate of barites and phosphate of lime.

66. It is an erroneous opinion of the nature of precipitates which has led to the doctrine of elective affinities, and to the construction of those tables which have so much engaged the moderns, and which are deceitful under an appearance of accuracy. As this doctrine is followed in the generality of chemical explanations, I feel it a duty to enlarge on the appearances which have produced it.

When a precipitate is formed by opposing one alkaline base to another which was already combined with an acid, it was concluded that the first liberated the second, and took its place in the combination: hence it has happened that the alkalis have been placed, in the order of their affinities, according to the mutual precipitations they are capable of producing.

A different method has been followed with the acids. When an acid, poured into the solution of

of a combination, produced a precipitate, it was concluded that it took the base from the other acid with which it had been combined. Hence a priority of elective affinity has been given to those alkalis which have the least tendency to solidity, and, on the contrary, it has been given to those acids which are most disposed to form solid combinations.

67. In all cases the precipitates which are formed arise from the same habitudes, whether they are produced by the addition of an acid or of an alkali to a neutral combination; all the difference depends on the habitudes themselves, and on the state of the forces in opposition to them.

Let lime, pot-ash, or ammonia, be added to a solution of phosphate of lime in its own acid, the same result will be obtained; the phosphate of lime, insoluble by itself, will regain this quality, because the acid, whose force was capable of dis- guising it, experiences a saturation which causes its action to cease: the only difference is, that all the lime will be reduced to an insoluble salt, and that the fixed alkali, or the ammonia, will pro- duce a soluble combination with the portion of the phosphoric acid exceeding that which forms an insoluble combination with the lime.

If, instead of an acidulous phosphate of lime, a solution of phosphate of lime in any other acid is used, there will be obtained, by means of the al- kalis or of the lime, a similar precipitate of phos- phate

phate of lime, and the combination formed, by the saturation of the acid employed as a solvent, will depend on the species of the acid, and on the species of the alkali.

Finally, if an acid, which has the property of forming an insoluble combination with lime, is poured into a solution of a calcareous combination, a precipitate is formed, analogous to those I have spoken of; but a part of the base remains in combination with the first acid, and an equilibrium is established between the force of cohesion and the dissolving force, until by the addition of an alkaline base all the action of the acid is overcome, as in the preceding instances.

All these phenomena are independent of the elective affinities, such as they have been considered, and if a classification of affinities by their relative force is desirable, it is not by the precipitations that the object can be accomplished; since these depend either on the increase of the force of cohesion by the act of combination, or on the diminution of the action which causes it to disappear, or renders it latent, and since they are modified by the respective quantities of the substances, by their condensation and by the temperature.

I shall add another example to those I have related respecting the contradictions to which the determination of the elective affinities by precipitations may lead.

Very

Very pure soda or pot-ash produce no precipitate in a diluted solution of muriate of strontian, but if it is concentrated, a precipitation ensues: if, therefore, it is examined in the latter state, it will be concluded that soda and pot-ash have more affinity for muriatic acid than strontian has: but this decomposes the sulphates and carbonates of pot-ash and soda; we must, therefore, admit an order of elective affinity for the sulphuric and oxalic (qu. carbonic) acids different from that of the muriatic acid.

Since barites when alone is much more soluble than strontian, and retains this property with muriatic acid, pot-ash and soda do not produce a precipitate with muriate of barites, in the circumstances in which the muriate of strontian afford it: for this reason it is requisite to attribute to it a different order of elective affinity, notwithstanding these different effects have a uniform relation with the solubility of the substances in the particular circumstances they may be placed in, and as soon as the force of cohesion becomes preponderant, it produces the separations which are adduced in support of this supposed election.

CHAP. IV.

Of the reciprocal Action of neutral Combinations.

68. IN the first chapter of this section I have considered acidity and alkalinity as two opposite qualities which mutually saturate each other; so that whenever their combination attains a neutral state, neither the acidity nor the alkalinity exercise any farther sensible action; this is not the case with the reciprocal action of the moleculæ, which continues to produce its effect; the properties arising from it are not, it is true, those of the two individuals; they have become common to the integrant parts of the combination; and, although they are derived from those of the elements of the combination, they are not a mean term, because its constitution has changed.

We have already seen (50), that one of these changes, that whose consequences I am about to examine in the reciprocal action of neutral combinations, consists in an increase of the force of cohesion, which must be the result of the approximation of the particles (5).

69. If the principles I have laid down are correct, acidity and alkalinity can no longer possess any influence on the reciprocal action of salts, in a neutral state, but all the phenomena they produce must depend on the properties which proceed from the reciprocal action of their integrant parts:

acidity and alkalinity when they have become latent, can only act in those circumstances in which they acquire a new liberty.

We have seen that the force of cohesion does not exercise its power solely on bodies which are actually solid, but that it is it, which pre-existing in that state, realizes it (9) : hence it follows, that in the mixture of liquid substances, the combinations which possess a force of cohesion capable of separating them, should, in fact, take place and be separated, for the same reason that water mixed with alcohol separates and becomes congealed ; but as in this instance a greater degree of cold is required to congeal the water, so the reciprocal action of the other substances must diminish the effects of the cohesion.

In the hypothesis examined in Chap. II., the force of cohesion of a neutral combination had to encounter not only the action of the water, but also that of the acid which united with the former; the dispositions of the combination, which the additional acid was capable of producing, caused a variation in the result, as well as the quantities of the substance : here the force of cohesion is single and proportionate to the solubility.

70. Let us review, therefore, the different conditions in which two neutral combinations may be found, and examine if the facts agree with the theory.

When a mixture is made of a soluble salt with base of lime, and a soluble combination of sulphuric

phuric acid, the latter, which has the property of forming an insoluble salt with lime, combines with it and precipitates, making an exchange of bases with the other acid: but sulphate of lime has much more solubility than sulphate of barites; if, therefore, a solution of sulphate of lime is mixed with a more soluble combination of barites, it makes another exchange of bases, and sulphate of barites is precipitated.

Supposing that the combinations are in a neutral state, the liquid only opposes the solvent action of the water to the precipitation, or the feeble action which the soluble combination can exercise on that which separates; the force of cohesion has not to contend with that of an acid, so that its effect takes place much more completely, and is produced in circumstances which would have been overcome by a weak acidity.

In fact, if oxalic acid is added to a salt with base of lime, a precipitate of oxalate of lime is obtained, much less abundant than if a solution of a neutral oxalate had been used, because the action of the acid allows only part of the oxalate of lime to be formed, but with an oxalate this obstacle would not have existed.

71. Hence it follows, that if the force of cohesion possessed by a combination is but slight, and if it only produces an insolubility easily overcome, it may happen that no precipitate is obtained by pouring an acid into the solution of a salt, although it possesses the property of forming, with

the base of the salt, a combination which would have been insoluble, if the action of the water had not been assisted by that of the acid ; but a complete precipitation of this base will be obtained, by adding a neutral combination of the precipitating acid to the salt formed by it : this is what takes place with sulphureous acid, which produces no precipitate from a salt with base of lime or barites, but which precipitates these bases in sulphites whenever it is employed in the state of a neutral combination ; a similar effect will be obtained if, in the preceding circumstances, the excess of acid is saturated.

In the same manner, phosphate of lime being easily soluble in the acids, no precipitate is obtained by pouring phosphoric acid into a solution of a salt with base of lime ; but if a solution of a calcareous salt is mixed with that of the phosphate of an alkali, the phosphate of lime separates and is precipitated.

It would be useless to accumulate in this place a greater number of examples : " on a review of " all the known decompositions arising from " complex affinities, it will be seen that it is always to those substances, which possess the " property of forming a precipitate, or a salt " which can be separated by crystallization, that " an excess of affinity superior to those opposed " to it has been attributed ; so that it may be foreseen by the degree of solubility of the salts " which can be formed in a liquid, which are the
" sub-

" substances, whose forces Bergman, and other learned chemists, have endeavoured to represent in symbolic tables, by always attributing " a superiority of affinity to the two substances " which can form a combination, insoluble with " respect to the quantity of the solvent."*

72. This effect of insolubility may be modified by some circumstances which must be attended to, especially when it is but slightly different in the combinations which are in action: these circumstances are the reciprocal action of the integrant particles of the two combinations, their respective proportions, and the changes produced by temperature in their comparative solubility.

Saline substances exercise a reciprocal action which augments their solubility: this effect is null or very small when the difference of the solubility is great; but it may become so strong between two salts, both of which have great solubility, as wholly to prevent crystallization. (31—32).

The result is varied by the proportions of the substances in action; thus, when that which has the greatest solubility is formed in the greatest quantity, it partly separates first; the combinations crystallize successively, according to the faculty possessed by the water of holding in solution the quantity of each at different periods of crystallization; a part of the least soluble salt acquires greater solubility by the action of the other;

* Recherch. sur les lois de l'Affinité.

so that a portion of it may remain in the uncrySTALLizable residue, while a considerable quantity of the most soluble salt crystallizes until they attain the proportions at which the reciprocal action prevents them equally from being formed; then a part of the first may still crystallize.

I have ascertained, by many examples, these successive effects of the reciprocal action of combinations, and of their proportions in the water which holds them in solution: at present I shall only relate a few of them.

73. If sulphate of pot-ash and nitrate of lime are mixed, in any proportions, the sulphate of lime which is formed separates by the excess of its insolubility compared with that of nitrate of pot-ash: sulphate of pot-ash and nitrate of soda, which differ less in solubility than the two preceding salts, will, by crystallization, yield a greater proportion of sulphate of pot-ash than of nitrate of pot-ash; but when the proportion of the first shall be diminished by the crystallization, nitrate of pot-ash will also be obtained, because the water remaining at this period is incapable of holding in solution the quantity of this salt which may be formed, and because the sulphate of pot-ash, on its part, is rendered more soluble by the action of the other salt: this result might have been obtained from the commencement of the crystallization by augmenting the proportion of nitrate of soda.

A mixture of nitrate of pot-ash and muriate of lime

lime yields also a result, in which the influence of the proportions is still more marked, because the two least soluble salts which can be formed, the nitrate of pot-ash and the muriate of pot-ash, differ but little in this property: either of these salts may also be obtained at the first crystallization by a little variation in the proportions of the nitrate of pot-ash and muriate of lime.

74. It sometimes happens, that, instead of simple combinations, that is to say, those formed of two substances, there are produced triple salts, or even those more complex; thus, when equal weights of sulphate of pot-ash and muriate of magnesia are mixed, or two parts of muriate of magnesia and one of sulphate of pot-ash, there is produced, by successive crystallizations, first sulphate of pot-ash; then a triple salt composed of magnesia, sulphuric acid, and pot-ash; after that, muriate of pot-ash; and finally, sulphate of magnesia. When equal weights of muriate of soda and sulphate of ammonia are mixed, the first salt obtained is a sulphate of soda and ammonia: in these cases, which seldom occur in non-metallic salts, it is equally obvious that the salts are separated in the ratio of their insolubility, modified by the proportions and reciprocal action.

75. The solubility of salts varies by a difference of temperature; but this does not follow the same progression in all of them. In some it acquires a considerable augmentation by an elevation of heat; in others it remains nearly the same. This condition,

condition, which determines the separation of salts, may therefore produce different effects according to the thermometric state; hence it happens, that salts whose solubility is nearly equal at one degree of heat, may, nevertheless, be easily separated, by producing a great change in the temperature, and, by making the effect of the proportions, and that of the difference of solubility, predominate alternately.

Nitrate of pot-ash and muriate of soda furnish us with a striking example of this effect. Near the freezing point nitrate of pot-ash has much less solubility than muriate of soda; but it is considerably increased by heat, and that of muriate of soda very little; so that the solubility of the latter, which was only about half that of the nitrate of pot-ash, comes to a degree at which it is equal, and finally at the boiling point becomes nearly eight times less. By boiling the mixture, therefore, the muriate of soda is made to crystallize at a high temperature, and then, by cooling, the nitrate of pot-ash is crystallized: the proportion of each salt is diminished alternately, and by repeated crystallizations they are both entirely separated.

76. It is generally supposed, that salts are formed in a solution such as they are afterwards obtained from it by crystallization; but the separation which takes place, according to the order of their solubility, and according to the proportions which act, shows that their parts exercise their

their reciprocal action equally, as I have supposed, (52). Nevertheless, when the attention is not directed to what passes in the liquid, but to the result alone, the common expression which supposes the existence of salts is convenient, and causes no difficulty: I shall therefore continue to use it.

77. The reciprocal action of saline combinations, which produces the uncrystallizable residues, is exercised at the moment of crystallization, as if the salts had pre-existed, or as if, after having formed those which are crystallizable, they had been immediately dissolved; so that the exchange of bases produces no difference in the result. But, although the effects of the reciprocal action of salts may be, in most cases, so slight that it may be overlooked, there are nevertheless some instances in which it is deserving of notice.

When sulphate of pot-ash is decomposed by muriate of lime, at first a quantity of sulphate of lime is obtained, less than would have resulted from the immediate combination of sulphuric acid and lime in the same quantity of water; it is from the same cause that, according to the observation of Guyton,* a solution of sulphate of pot-ash, muriate of pot-ash, &c. poured into lime water, rendered milky by water impregnated with carbonic acid gas, instantly cause the precipitate to

* Mem. de Scheele, part II. note to page 18.

disappear;

disappear; and also that no precipitation takes place when water impregnated with carbonic acid is poured into a mixture of lime water and a solution of these neutral salts.

This effect, which is very slight, and often imperceptible, in salts which have a considerable force of crystallization, because the crystallizing force of the one salt may overcome the action of the other, (72), becomes much greater, when both have but little force of cohesion, such as the sulphate of soda and the nitrate of soda, which, in certain proportions, are almost wholly deprived of the faculty of crystallizing: consequently the uncry stallizable salts produce a great effect on those which, in themselves, have but a weak disposition to crystallize; but the division of the water which may take place between the salts and produce precipitations, (33), must be distinguished from their reciprocal action.

78. It is, therefore, the same cause which produces the separation of the combinations in complex affinity, and in that wherein two acids endeavour to combine with one base. The only difference between them is, that in the one case there is a neutralization; and in the other, an excess of acid which unites its action with that of the solvent: in fact, whenever this excess of acid is overcome, either by an alkali or by evaporation, the difference disappears.

By the action of this excess of acid, the separation, which would have been produced by the disposition

disposition to combination, is prevented, or is not so complete as in a complex affinity.

It may also affect the proportions of the constituent parts of some combinations (65); thus the precipitates or solid combinations obtained by the action of neutral salts, are in a much more uniform state than those which have had an excess of an acid or an alkali to conquer.

That which has been advanced on the competition of two acids to combine with one base, and on the action of two saline combinations, must be applied to the action of all acid and alkaline substances, and of all the combinations formed by them, however numerous the substances in action may be. An acid power, and an alkaline power, must in all cases be distinguished; if these two powers are in equilibrio, that is to say, if there is a neutralization, what has been said on the reciprocal action of the integrant parts of neutral combinations is applicable to them.

If, on the contrary, there is an excess of one of the two powers, their action is explained by what has been advanced, on the action of two acids on one base (52).

79. An erroneous opinion of affinity has introduced many suppositions in the results of the reciprocal action of saline substances; thus from having obtained one description of salt by a first crystallization, it was concluded that a complete exchange of the base had taken place between the two acids, while, opposite combinations might succeed,

succeed, or be formed, in the first instance, according to the proportions of the substances brought into action at the period of crystallization (73), and contradictory inferences might consequently be drawn from the results of an operation, according to the circumstances which accompany the crystallization.

The effects of saturation, which are a result independent of solidity or liquidity, have been confounded with those of the reciprocal action of their integrant parts, and of the force of cohesion peculiar to them, and attempts have been made to represent, by numbers, the force of acids which could select their bases, notwithstanding the separations only take place in the ratio of the solubility of each combination.

This solubility is not an absolute property, but depends on the relation of the action of water with the force of cohesion ; so that if water is not the solvent, or if it contains any other substance which modifies the action, the effects are different. (See *Note I.*)

The preceding phenomena are in no respect different from those we have analysed (*Sect. I. Chap. III.*), in which we considered only the mutual action of the substances in solution ; so that the separations and precipitations made by an exchange of bases, are an effect of the force of cohesion peculiar to the combinations, and which is simply modified by their reciprocal action : the acidity and alkalinity which have become latent, only

only contribute in an indirect manner; but the theory I have advanced, supposes that the state of saturation experiences no change from the mutual action of saline substances; this I shall endeavour to establish in the following chapter.

CHAP V.

*Of the comparative Capacity of Acids and of
Alkalies for Saturation.*

80. THE acids and alkalies differ from each other, by the actual quantity found, either in the liquids which bear their name, or in the combinations they form; but the capacity of saturation, which is the measure of the power of acids and of alkalies, cannot be determined until their real quantity is known.

In general, since chemical action is varied by the quantity, it is of consequence to determine the actual quantities of each substance which can be brought into action. The composition of combinations cannot be ascertained but by the proportion of their elements, and to be able to fix them, it is in most cases necessary to know that of the agents employed: the explanation of the phenomena to which these combinations contribute, requires the same knowledge.

The determination of the proportions of a substance

stance which can be made to act, or which exist in a combination, is therefore, the foundation of all chemical enquiries : the object of all the methods, of all the processes, is to arrive at it, and this object ought never to be lost sight of by chemists.

As acids and alkalis are the principal agents employed in analysis, particularly in mineral analysis, the knowledge of their actual quantity in the liquids which bear their name, or in the combinations which they form, is of the most material importance. But as the alkalis, with the exception of one, have a fixity which allows their quantity to be more easily discovered, it is the acids from which it is most difficult to obtain a result sufficiently accurate.

These motives have induced me to enter into some details on the methods which have been employed to determine the quantities of real acid in liquids, or in solid combinations.

Kirwan is the chemist to whom the most important labours on this subject are owing, not only for the perseverance he has employed but for the authority of his name ; and in selecting his results, as being the most entitled to confidence, for the subject of the following considerations, I shall endeavour to demonstrate their uncertainty, and in so doing, believe I shall forward the views of this skilful chemist.

At first, Kirwan endeavoured to determine the quantity of *real* acid which entered into combination,

nation, either with the water of the common acids, or with alkaline bases; for this purpose he made use of muriatic acid gas. But this gas contains an indeterminate quantity of water and it might lose this water, either wholly or in part, when the combinations it had formed were urged by fire. In proof of this, when muriate of soda is decomposed by sulphuric acid, and when the mass has undergone the action of heat for a long time, the disengagement of muriatic acid gas is restored by the introduction of water, which, by its combination and vaporization, favours this disengagement, as it does with the carbonates. This quantity of water is a sufficient cause of uncertainty in a substance which passes from the gaseous to the liquid state, or which enters into solid combinations.

To determine the quantity of real acid in the combinations of the other acids, he supposed that the alkaline bases received an equal quantity of each species of real acid: this supposition led him to conclusions far from the truth; but observation produced knowledge, and his last work was fixed on a surer foundation.

In the work in which Kirwan makes known the mature fruits of his long observations,* he first describes those he had made on the dilatation experienced by sulphuric acid, nitric acid, and muriatic acid, in the passage from 8° of Reaumur's thermometer to 16.9°; an exteat of the thermo-

* Bibl. Britan. tom. xiv.

metric scale, sufficient for chemical observations : and, from these observations, he investigated the quantity of acid in the acids of different specific gravities, at a temperature of 60° Fahr. Let us examine how he proceeded : 1st. to measure the dilatations produced by the elevation of temperature ; 2d. to determine the quantity of real acid corresponding with the different specific gravities.

He examined the dilatation of sulphuric acid, at three different degrees of specific gravity : the specific gravity of the first was 1.856, it gained by cooling, or lost by heating 0.00068 in each degree between 60° and 70° of Fahr. and 0.00043 for each degree between 60° and 49° : the second, whose specific gravity at 60° was 1.700, lost or gained 0.00036 for each degree of temperature between 60° and 70° ; and 0.00051 for each degree between 60° and 50° : the specific gravity of the third was 1.333, it lost or gained 0.00043 between 60° and 70° and 0.00034 between 49° and 60°.

That which makes me apprehensive of some inaccuracy in these observations is that the results do not follow a regular gradation, though no reason can be perceived for this difference. The second acid acquired less specific gravity than the first and third, between 70° and 60° ; but it gained more at the inferior degrees.

The author also examined the dilatability of nitric acid, according to its concentration by different degrees of heat, and he observed that the greater its concentration the greater was its dilatability,

dilatability, and that it was more so at higher than at lower degrees of temperatures; which will explain the observations of Proust, who remarked, that in distilling concentrated nitric acid, so that a portion might be left in the retort, the residue had less specific gravity than the part which passed in distillation, and the greater the concentration of the acid, the more easily was it distilled.*

Kirwan remarked that the expansibility of muriatic acid was greater than that of nitric acid of the same specific gravity; but this acid possesses a peculiar property.

81. Sulphuric acid and nitric acid, by their combination with water, experience a concentration, which occasions the specific gravity acquired by the mixture to differ from that resulting from their primitive specific gravities; while the specific gravities of muriatic acid mixed with different proportions of water, corresponds exactly with that resulting from the weights of the water and the acid, and which he designates by the denomination of mathematical specific gravity.

This property, which distinguishes the muriatic acid from all the combinations, in which it is observed that the volumes of the elements experience a condensation, unless there is a particular cause for a contrary effect, probably depends on the muriatic acid gas, in its passage to the liquid state, experiencing so much condensation from the

* Journ. de Phys. Messid. An. X.

great quantity of water which is required, that an increase in the proportion cannot exercise a force on it which will produce a sensible alteration in the state in which it is found,

Kirwan has formed a table, by combining the effect of the condensation of sulphuric acid and nitric acid with the differences of the specific gravity, to deduce the quantity of real acid; and to determine this, he has considered as real acid, that contained in sulphate of pot-ash, in nitrate of soda, and in muriate of pot-ash strongly dried; since muriatic acid experiences no condensation by the action of water, it does not require tables different from those of its specific gravity.

It must either be supposed that the acid contains no water in the desiccated salts, or it must be neglected; it must also be supposed that the quantity of the base is well ascertained: in each computation therefore, with whatever care it is made, it is obvious that it must be accompanied with some uncertainty, which is disseminated through all the results.

A table of this construction may be used to compare the quantities of acid, in the same species of acid, according to its different specific gravities, or the quantities of acid in a different species; its utility is undoubted in many cases, but it does not appear to me to be useful for determining those elements of saline combinations, for which its author particularly intended it. It seems to me, that its use in this case has no superiority over

over the direct method employed by chemists : in effect it is always requisite to begin by determining the proportion of the base ; after that, it is either saturated by a quantity of acid, the real acid of which is given in Kirwan's table, or the process goes on to crystallization, and then to a strong desiccation, to ascertain the quantity of water which heat is capable of separating from the combination ; the weight which the base has acquired and retains, notwithstanding the heat, is then considered as the real acid, and that lost by the combination during its desiccation, is considered as water ; but as the determination of the water is always useful, chemists can seldom dispense with this last proof ; nothing now remains but to know, whether it is proper to depend upon the table of Kirwan, or to consider as real acid, the weight acquired by a well-determined base, and retained by it after strong desiccation : it appears to me, that there is at least as much exactness in trusting to this augmentation of weight ; for Kirwan's table only fixes the quantity of real acid by an examination made with a base : it therefore has, of necessity, all the uncertainty of this determination, and also, all those arising from a determination founded on a multiplicity of data.

I see no reason which could have determined Kirwan in the choice of the salts he has employed ; it appears to me, that the combinations most proper to obtain the object, are those with a base which does not evaporate when pushed to desic-

cation, and which do not easily attack the vessels in which this previous operation is performed, to ascertain the quantity ; such are barites, strontian, and lime : these bases have also the advantage of forming insoluble combinations with several acids, by which means the quantity of these acids in other combinations may be discovered ; but nitric acid, which, with alkaline bases, forms only soluble salts, readily decomposed by heat, presents difficulties not easily overcome ; and Kirwan acknowledges that his estimation of the nitrates is not so accurate as that of the other salts.

82. The preceding considerations show, that the tables by which Kirwan fixes the elements of saline substances, cannot be regarded as strictly correct. Guyton has proposed a method of verifying the proportions which they suppose, which appears to me to unite simplicity with an accuracy to which no difficulty can be opposed : " This " method consists in comparing the results of the " experiment and of the calculation, in order to " obtain their agreement in the very sensible effect " of the excess or defect of one of the substances, " after the reciprocal decomposition."*

Guyton observes, in consequence, that when an exchange of base takes place between two salts, the result of the mixture must either be neutral, with an excess of acid, or with an excess of base ; and that by rendering the decomposition of one of

* Ann. de Chem. tom. xxv. p. 292—Mem. de L'Instit. tom. ii.

the

the salts complete, the same results should be obtained by calculation as by experiment: he therefore examines what should take place, according to Bergman's proportions, when muriate of barites is mixed with sulphate of soda, and he shows that there ought to be a considerable excess of acid; nevertheless the mixture remains in a neutral state; whence it must necessarily be concluded that the proportions of Bergman are distant from the truth.

Guyton makes a similar observation on the mixture of nitrate of lime and sulphate of pot-ash, according to the proportions of an amended table, published by Kirwan in 1791; and of sulphate of soda and muriate of magnesia.

Richter appears to have been the first chemist who attended to the remarkable property of saline combinations, of not experiencing a change in their state of saturation, when they are blended in the same solution. A summary of his opinions will be found in a note, which I have extracted from Fischer's translation. (*Note II.*)

I am convinced by my own experiments, that the state of saturation does not undergo any change, when different neutral salts are mixed, which produce precipitates, or from which, salts which have exchanged bases are obtained by crystallization, provided metallic salts are not employed, in which this correspondence does not appear to exist. (*Recherches sur les lois de l'affinité.*) I have repeated these experiments with different

different combinations of sulphuric, sulphureous, phosphoric, oxalic, acetic, and tartareous acids, and I have only perceived a slight change with the phosphates of pot-ash and soda, which left a very feeble acidity in the liquid on being mixed with the soluble salts with a base of lime, which only shows a disposition in the phosphates to take an excess of base, such as is in fact observed in some of the combinations of the phosphoric acid.

83. I have employed the methods of Richter and Guyton, 1st. with a mixture of sulphate of pot-ash and of muriate of barites, following the proportions of Kirwan's last tables: sulphate of pot-ash contains, according to these tables, 82.48 of acid to 100 of the base; muriate of barites, 31.80 of acid to 100 of base, and muriate of pot-ash 56.30 of acid and 100 of base: to enable the exchange of bases to take place without the neutral state being changed, there should be a quantity of muriatic acid sufficient to saturate 100 parts of pot-ash, that is to say, 56.30; now 56.30 of muriatic acid would saturate 177.04 of barites; but 177.04 of barites would require, according to the table, 88.52 of sulphuric acid, and there is no more than 82.48 in the sulphate of pot-ash, or there could only be, in the muriate of barites, 164.96 of barites instead of 177.04 with 56.30 of muriatic acid.

2d. With a mixture of sulphate of soda and muriate of barites: to decompose them by an exchange of bases, it requires that there should be in

in the sulphate of soda 115.42 of acid, instead of 127.65, or that in the muriate of barites there should be 253.36 of barites, instead of 230.84 with 73.41 of acid.

3d. If the same calculation is applied to a mixture of nitrate of lime and sulphate of pot-ash, it will be found that 100 of lime requires 179.50 of acid, instead of 143; so that 96.50 of sulphuric acid are deficient in the proportions given to produce the saturation of all the lime, or else this base must be in a less proportion in the nitrate of lime.

4th. The mutual decomposition of sulphate of ammonia and muriate of barites offers still greater disproportions: to enable the sulphate of ammonia and muriate of barites to exchange their bases, and preserve the state of neutralization, sulphate of ammonia should contain 268.86 of acid, instead of 383.80, or muriate of barites should have 767.60 of barites, instead of 537.73 with 171 of acid.

If part of this difference could be removed in the valuation of the muriate of barites, the greatest part must certainly be attributed to that of the sulphate of ammonia, in which a proportion of acid, much too strong, is found, as is shown by other considerations; and in his first table, Kirwan fixed it in the proportion of 100 to 95, a proportion much too weak in an opposite sense.

These deviations are too considerable to be explained by supposing a proportion of acid more or less

less strong, in the sulphate of barites which is formed: on the other hand, this supposition, which is without foundation when the exchange takes place between two salts in a neutral state, cannot be applied to the mixture of nitrate of lime and sulphate of pot-ash.

When this experiment is made with sulphate of ammonia, the slight acidity possessed by this acid after crystallization must be previously removed; but the quantity of ammonia necessary to this end is so small that it cannot sensibly change the proportions of the elements of this salt.

84. The preceding observations appear to me to lead necessarily to this consequence, which I have only hinted at in my Researches into the Laws of Affinity, but which is absolutely established by Richter, that is to say, that the different acids follow correspondent proportions with the different alkaline bases, to acquire a neutral state of combination: this consideration must be highly useful in verifying the experiments made on the proportions of the elements of salts, and also in determining those which have not yet been experimentally ascertained, as well as in the establishment of the most certain and easy method of accomplishing this object, so important to chemistry; but, 1st. it is only applicable to those saline substances whose decompositions can be effected without the formation of triple salts, or at least the comparison can only be made on combinations which do not yield triple salts: 2d. only those substances

substances can be admitted into this comparison which are capable of forming neutral combinations, a property which I have fixed as the distinctive character of acids and alkalis: for this reason, sulphate of alumine must be excluded, not only because alumine does not produce complete saturation with acids, but also because it requires the aid of an alkali to form sulphate of alumine, and even then this salt retains an excess of acidity: So the combinations can only be made use of in a neutral state, because an excess of acid or alkali cannot be appreciated without the intervention of a substance which would render the result too complicated.

Laying aside these exceptions, nothing more is required but to determine with care the proportions of an acid with the different alkaline bases; it will then be sufficient to ascertain the proportions of a single combination of each of the other acids with an alkaline base, taking that which is the most convenient for experiment, and an easy calculation will give the proportions of all the others.

85. This exact correspondence of the proportions of an acid with different bases, and of a base with different acids, is connected with the theory I have laid down on the mutual action by which the acids and alkalis produce mutual saturation; it proves that this mutual action is not only a force which exists in a certain degree between two individuals, but that it is the same in all

all the substances endowed with acidity or alkalinity, or that its effects are only varied by the intensity with which substances possess it. Since, of all the chemists who have preceded me on this subject, the opinion of Kirwan has the greatest analogy with that I offer, I thought it right to pause to discuss the differences which at first appear slight, and which have nevertheless led to opposite results.

86. In classifying the relative affinities of alkaline bases, Kirwan maintains, 1st. that the quantity of real acid necessary to saturate a given weight of each of the bases is in the inverse ratio of the affinity of the bases for the acid : 2d. that the quantity of each base necessary to saturate a given quantity of each acid, is in the direct ratio of the same acid with the base; so that, on one hand, a greater affinity requires a less quantity of one of the saturating principles; and on the other, it requires a greater quantity, and it is by means of this contradiction that he supports the existence of the elective affinity, and estimates the force independently of the quantities in action, notwithstanding he has acknowledged their influence; he afterwards, on the determinations of the elective affinities, establishes the results of the double affinities, and the balance of the quiescent affinities and the divalent affinities. Thus, by ingeniously dividing the forces which produce two combinations into quiescent forces and divalent forces, he no longer admits into the comparison

rison of these forces, the consideration of the quantities which act, and he considers, as a uniform force, the affinity of an acid, measured by the quantity of an alkaline base which it can saturate; so that the decomposition is completely made, as I have just observed, accordingly as one calculated force can overcome another: but I have shown, (75), that whenever the exchange of bases is not excited by a considerable force of cohesion, the salts formed in the mixture are varied by the proportions of the opposite substances in action.

This learned chemist endeavours to support his theory of quiescent and divellent affinities, as determined in his method, by some examples, in which he finds that the numbers affected in each affinity are satisfactory for the combinations which are formed; but if any value is given to the numbers chosen to represent these effects, I shall take, even from his table, those which cannot bear this proof; thus, the affinity of sulphuric acid determined by the quantity of pot-ash which it can saturate, is represented by 121, and that of muriatic acid by 314; which gives for the quiescent affinities 435, when sulphate of pot-ash is mixed with muriate of barites; and the divellent affinities of sulphate of barites and muriate of pot-ash give only 377, so that no decomposition should take place; yet, notwithstanding, it is complete: in the same way, when muriate of strontian and sulphate of pot-ash are mixed together,

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the quiescent affinities are 337, and the divellent affinities but 315.

87. Chemical action is reciprocal; affinity is proportionate to it; saturation is a common term to all the acids and all the alkalis: to compare the saturating action of the acids with a base, it is necessary to compare the quantities of each acid required to produce the same effect, that is to say, the saturation of the base: the affinity of two acids for a base must, therefore, be considered as being in the inverse ratio of the quantity of each of the two acids which is capable of saturating the base, as I have maintained in the first chapter: if the alkaline bases are compared, they must be considered in the same way, and the base which, with the smallest quantity, shall produce saturation, must be that which exercises the most energetic action, which has the greatest affinity: finally, we have seen that the relations of these two forces are preserved in all the combinations formed by the acids and the alkalis.

If the observations which I have offered prove that a capacity for saturation is the measure of the power, or of the affinity, they exercise as acids, we must form an opinion of this comparative affinity, very different from that laid down in the tables of affinity.

The fluoric acid, according to the experiments of Richter, must be the first acid in power, since 1000 parts saturate 1882 of lime.

The phosphoric should follow after: according to

to Vauquelin, 1000 parts saturate 1440. Then comes the muriatic acid, and next the sulphuric and nitric, the difference of which has not been well ascertained.

On applying the same method to the alkalis, ammonia takes the first place, according to Kirwan, whose experiments appear to me much more exact than those of Richter: magnesia and lime follow; and then soda, pot-ash, strontian, and barites.

I do not take carbonic acid into this comparison, because the carbonates employed by Kirwan in his experiments had nearly all a variable excess of alkali; with respect to the other acids, the proportions of the elements of their combinations are determined in so few cases, and with such imperfection, that they cannot be employed to ascertain their places in the order of affinities, although they may follow the same progression in the quantities of the different bases necessary to their saturation.

88. To accommodate this result to the received order of affinities, it is necessary to seek, in the habitudes of the substances which combine, and in the conditions in which they may be found, the natural explanation of the facts which have led to conclusions so opposite: it is to the force of cohesion alone, the effects of which have been confounded with those of elective affinity, that I, in this place, attribute the cause of this difference, without examining also the circumstances which

fix

fix the proportions of combinations. The sulphate of barites possesses a considerable force of cohesion compared with the combinations which may be rendered soluble by water, and with respect to the acids, it is in the same situation as alumine which has experienced a strong concentration, as in porcelain or in the sapphire. Would it not be said, if alumine was only known in this state of condensation, that sulphuric acid had no affinity with it? Does not the alkali combined with silex in glass, become insoluble by the acids which would have separated it so easily, if the force of cohesion acquired by this combination was not superior to their action?

When it is asserted, that sulphuric acid has more affinity with barites than the other acids have, no notice is taken that this acid itself, unless it be greatly concentrated, or its action be assisted by heat, has no more action on the sulphate of barites than the other acids, and that consequently its affinity has no more energy against the force of cohesion of the sulphate, which must not be confounded with the power of saturation, or with the opponent power of alkalinity.

To consider barites as endowed with a much stronger affinity for carbonic acid than ammonia, is to assert that a much greater force is required to overcome the resistance of the elasticity of a small quantity of elastic fluid, than of a great quantity.

89. Whatsoever may be the opinion retained respecting elective affinity, we cannot refuse to acknowledge a striking relation between the capacity of the acids for saturation and the invariable proportions of the different alkalis which can saturate them; and it must be agreed, that these properties bear relation to the affinity of the acids for the alkalis; whence it may be concluded, that there can be but a trifling difference between the affinity of sulphuric acid and that of muriatic acid for barites, if the superiority of the latter is denied; nevertheless, the first is supposed to have the greatest affinity for this base, and the muriate of barites is easily decomposed by acetite of lead and by nitrate of silver, although these oxides have so little action on the acids, with which they form these soluble combinations, that they cannot completely saturate their acidity. To explain these precipitations, the excess of force of the muriatic acid above that of the acetic acid, is balanced by the difference between the affinities of these oxides for the different acids: this difference is considered conclusive if numbers are found which correspond with the supposition, however remote they may be from representing the real properties, such as the capacity for saturation; finally, every consideration of the insolubility of the precipitates is neglected, although in the end it is brought into the explanation of their properties.

What I have advanced in this section on the affinities,

finities, is not applicable to the action of several acids on a base, or of several bases on an acid, when there is a change of temperature which causes the force of cohesion to vary, and particularly when there is a difference of dilatability, which also increases by the heat disengaged during chemical action, or which is applied.

Having examined the effects of the opposite action of liquidity and solidity; of acidity and alkalinity; I shall proceed to the changes produced by caloric in the reciprocal affinity of the moleculæ of bodies, and in that which forms combinations.

SECTION

SECTION III.

Of Caloric.

CHAP. I.

Of the Effects of Caloric independent of those of Combination.

90. THE cause of heat, which I denominate *caloric*, whatsoever may be its nature, has a power so extensive, and exercises it in circumstances so varied, that it is of importance to appreciate truly each of its effects, that they may be taken into the account in the more complicated phenomena. I shall, therefore, begin by detailing the most elementary opinions on the changes produced in bodies which are submitted to its action alone.

When several bodies, at different degrees of heat, are brought into contact, a temperature is produced, more or less rapidly, which is uniform and common to the whole system.

If water, at the temperature of zero, but still liquid, is mixed with an equal weight of water at 60° , the mixture acquires a heat of 30° : so that

caloric is distributed among homogeneous substances in the ratio of their quantity.

91. The division of temperature does not follow the same law when the bodies are of a different nature, or in a different state. For example, experiment proves that a metal plunged into an equal weight of water of a higher temperature, gains more degrees of thermometric heat than the water loses, and this takes place in different proportions for each species of metal.

Hence it must be concluded, that the caloric which augments the temperature of the water one degree, would raise that of an equal weight of metal in a greater proportion, and that there would be a different increase for each metal.

92. An analogous disposition is manifested in all bodies; they take different temperatures by the acquisition of the same quantity of caloric. This disposition may be measured; for this purpose the quantity of caloric necessary to raise the ponderable unity of a body, one degree of temperature is taken as the unity of caloric; to this the other bodies are compared. The quantity of caloric necessary to raise the temperature of a ponderable unity of another body one degree also, is determined by experiment. This comparative quantity of caloric is called the *specific caloric* of a body. The name of *capacity for caloric* has also been given to this property of bodies of requiring different quantities of caloric to pass through the same degrees of temperature; considering it as a comparative

comparative power which they possess, I shall use these two expressions indiscriminately.

An example will make this more clear: let us suppose that a body whose temperature is equal to zero is plunged into an equal weight of water at 50° , and that the temperature of the mixture, having attained the state of equilibrium, has become 30° : the water by communicating part of its caloric to the body has lost 20° of its temperature, and the same quantity of caloric to which this loss is owing, by passing into the immersed body has raised its temperature 30° .

It is evident, that if the same quantity of caloric produces different changes of temperature, in two bodies of equal weight, that which has experienced the greatest alteration, requires the least caloric to make a difference of one degree, and that this quantity will be less in the same proportion as the variation shall have been greater: therefore, the specific calories of two bodies are in the inverse ratio of the variations of temperature produced by the same quantity of caloric in two equal weights of these bodies. If one of these two bodies was water, its specific caloric may be taken for unity, and it will be easy, from what has been just said, to determine the specific caloric of the other body by comparing it with this unity.

By returning to the preceding supposition, it will be seen that the specific caloric of the body is to that of an equal weight of water as 20 to 30,

or as 2 to 3; that is to say, that taking that of the water as 1. that of the body will be $\frac{2}{3}$.

From what has been advanced the following rule may be established: *If, having immersed a body into an equal weight of water, of a different temperature, and having suffered the equilibrium to be established, a fraction is made, which has for its numerator the variation of temperature experienced by the water, and for its denominator the variation experienced by the body; the sum of the specific caloric of the body will be expressed.*

If a weight of water equal to that of the body has not been employed, the result must be multiplied by the weight of the water, and divided by that of the body.

93. That which has been just stated is true only when the bodies subjected to experiment have remained in the same state; but if, being preserved from all combination, they pass from the solid state to the liquid state, or *vice versa*, other phenomena are produced: water offers a remarkable example.

When any weight of solid water, or ice, whose temperature is the thermometric zero, is mixed with an equal weight of water at 60° , the result is double the weight of the water, at the temperature of congelation.

This phenomenon could not have been expected after what has been said before relative to the division of temperature. On examining it, alone, we find that solid water has become liquid without

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an increase of temperature, and that the liquid water has lost 60 degrees. The caloric, therefore, which kept it at this temperature has been entirely employing in liquefying the ice, and the true conclusions from this fact are the following:

Whenever ice passes into the liquid state it combines with a quantity of caloric capable of raising an equal weight of water from zero to 30° of the thermometer.

At the temperature of zero, solid water differs from liquid water in this, that it also contains as much caloric as is capable of raising the same weight of water from the temperature of zero to 60°; but this caloric, by its combination, has lost its power on the thermometer.

From this it is easy to conceive how it happens, that, in a temperature above congelation, the thermometer surrounded by pounded ice remains constantly at zero, and does not begin to rise until all the ice has taken the liquid state.

94. Liquefaction is not the only circumstance in which caloric loses its power on the thermometer by combination.

A thermometer immersed in water, while it is heating, shows the successive degrees of temperature acquired by the water, as far as ebullition, but at this degree it remains stationary; the continued addition of heat only accelerates the reduction of the water into vapour, but produces no variation of the temperature; the thermometer, removed into the vapour, is still stationary while any

any water remains in the liquid state; but as soon as its conversion into vapour is completed, the caloric which continues to combine exerts its thermometric power, and the temperature is raised.

This fact proves, that when water passes from the liquid state to that of vapour, caloric is accumulated in it with the loss of its thermometric power, as in liquefaction; the caloric which disappears in this manner, would, according to the experiments of the celebrated Watt, have raised an equal weight of water, not reduced into the vaporous state, 943° Fahr. or nearly 500° of the centigrade thermometer.

95. The caloric thus combined re-appears, producing its thermometric effects, when, for example, the vapour of the water, transferred into a recipient, gives up the caloric by which it acquired its state of vapour and resumes the liquid state; its réduction into a liquid continues until the receiver has acquired the temperature of ebullition.

In the same manner, water, which having been exposed to cold, has, without ceasing to be liquid, acquired a temperature below that of ice, causes the thermometer to rise, at the moment at which it is solidified. The quantity of ice formed at this instant depends on the proportion of water which remains liquid, and can absorb the caloric abandoned by the other portion, and on the degree of cold existing in the whole mass: so that by knowing

ing the weight of water, and the degree of cold it has attained, the quantity of ice that will be formed may be determined.

96. Analogous effects take place in all bodies, when, by the sole influence of caloric, they pass from one to the other of the three states of solid, liquid, and vapour.

The caloric which is accumulated with the loss of its power on the thermometer, has been called *latent heat*, or *latent caloric*, and that which produces thermometric effects has been designated *free caloric*.

97. When a body is exposed to an atmosphere hotter than its own, it is heated insensibly until all its moleculæ have gained the temperature of the surrounding fluid; but if this body is a mass of ice in a state of temperature immediately preceding that of liquefaction, the moleculæ which form the exterior layer of it will combine with the caloric and dissolve into a liquid; the next layer will liquefy in its turn; at each operation the caloric which liquefies the ice becomes latent, and loses the power of changing the temperature of the nucleus; it remains, therefore, constantly at zero; but at lower degrees, like other bodies, it takes a uniform temperature.

Let us conceive a space closed on all sides by a boundary of ice of the temperature of zero; there will be no communication between the interior and exterior; the surface of the ice presenting on each side limits beyond which the caloric cannot act,

act, the interior layers will be liquefied until they have exhausted the caloric which raised the interior temperature above zero, and, beyond that, liquefaction will not continue.

98. By these considerations we are led to estimate the quantity of caloric, disengaged during any phenomenon whatever, by a method different from that which has been shown (92): it will be sufficient if the phenomenon takes place within the enclosure of ice; by carefully collecting all the water which has been formed, it will indicate the caloric disengaged, and which has become latent by the liquefaction of the ice.

To bring the result of this proof to the unity of caloric already established, it is only necessary to multiply the weight of the water by 60, and the quantity of water will be given, whose temperature could have been raised one degree by the caloric disengaged.

The quantities of caloric eliminated during the cooling of a body are comparable to those which are disengaged during a chemical phenomenon, by means of the weights of water, the temperature of which they are capable of augmenting by one degree, for they are directly proportionate to these weights.

99. To obtain precision in these experiments, an instrument has been devised called a *calorimeter*. To the experiments made with this instrument by Lavoisier and La Place, are owing the most correct information on the effects of caloric, and

and the most exact theory of heat. This important work is my principal guide.*

The calorimeter is to be considered as composed of two concentric cavities, separated by a metallic partition, each containing pounded ice.

It is of importance that the exterior ice should be always at the point of liquefaction, for the purpose of keeping the interior ice at the temperature of zero.

The latter must be moistened before it is put into its place, that the water it retains at the end of the experiment may not weaken the result.
(Note III.)

100. To determine the capacity of a body for caloric, a ponderable unity elevated to a known temperature is placed within the interior cavity, the water arising from the liquefaction of the ice by the caloric communicated by the body subjected to experiment, during its passage from the given temperature to the freezing point, is carefully collected by means of a cock; the experiment, therefore, determines the quantity of caloric disengaged from the ponderable unity of this body; the temperature of the body is lowered a certain number of degrees to assume that of the ice; the disengagement of caloric corresponding to the variation of one degree is obtained by dividing the whole quantity disengaged by the number of degrees.

* Mém. sur la chaleur, Acad. des Sciences, 1780.

If the mass of the body submitted to experiment was not equal to a ponderable unity, the result is divided by the weight of the body, and the result, corresponding to a ponderable unity, is obtained.

101. If the elements made use of in the method (92), are compared with those of the actual determination, it will be seen that they are the same, and that the two methods lead to the same results; nevertheless, they differ in some circumstances which, in almost all cases, give the one much advantage over the other.

The method by mixtures requires that the effect of the vessels made use of should be taken into the results, and also the dissipation of the heat communicated, either to the atmosphere or to surrounding bodies, during the time the temperature of the mixture is acquiring uniformity: the difference of the specific gravity of the substances, such as mercury and water, is an obstacle which renders the equilibrium of the temperature difficult to obtain; the solvent action exercised by water on some bodies, complicates the result, and the difficulty of separating the effects becomes insurmountable when a combination is formed, or if there is a change of the constitution, as in combustion and respiration: finally, gaseous substances can only be employed in such small quantities, that in cases of that description this species of proof becomes entirely illusory.

The use of the calorimeter only requires an easy correction,

correction, that of the effect produced by the capacity for caloric of the vessel which contains the liquid bodies submitted to experiment: it is calculated to ascertain the caloric disengaged during all chemical phenomena, as well as that which quits a body while it cools.

It is nevertheless difficult to ascertain, by its means, the specific caloric of gazeous substances, because it is necessary to employ considerable volumes to liquefy a certain quantity of ice: with this view, a determinate volume is passed into a kind of worm contained in the calorimeter; the temperature given to it is observed by means of a thermométer placed in the conducting tube, and that which it retains on being removed from the apparatus; the caloric it has lost is estimated by the quantity of ice it has liquefied. Although the experiments on gazeous substances have not been made with that precision the authors intended to give them, their first results may be considered as much closer approximations than those obtained from mixtures.

102. The preceding observations explain the considerable differences to be found between the determinations of Crawford, who used the first method,* and those of Lavoisier and La Place. We are no longer surprised at the deviations of Crawford, who in his first enquiries attributed to oxigen gas, a capacity for caloric 87 times greater

* On Animal Heat.

than

than that of water, and who in his subsequent experiments reduced it to 4.749, while the latter found it to be only 0.65;* and although they have proposed this conclusion with much diffidence, it must nevertheless inspire more confidence than that of Crawford.

103. We have seen that in the modifications of temperature produced by mixtures, the caloric is distributed in the ratio of the capacities and of the quantities, and that in the changes of the state of bodies, it accumulates or is manifested in such a manner that, in the inverse changes, the bodies regain the same quantity of it. A similar effect takes place in the successions of those combinations which are accompanied by an absorption or disengagement of caloric; on these considerations, the authors of the Memoir on Heat have established the following principles:

If, in a combination, or any change of state whatever, there is a diminution of free heat, this heat will wholly re-appear when the substances return to their first state, and vice versa: if, in a combination or change of state, there is an augmentation of free heat, this new heat will disappear on the return of the substances to their primitive state.

In generalising this principle, all the variations of heat, whether real or apparent, experienced by the system of a body on changing its state, are re-

* Recueil de Mém. par Seguin. tom I.

produced

produced in an inverse order, whenever the system returns to its first state.

104. Caloric produces another effect on bodies whose connection with the changes of temperature must be attended to: it dilates them and augments their volume.

The dilatation which bodies experience by a given elevation of temperature is much more considerable in elastic fluids than in liquids, and in these than in solid bodies.

Liquids not only differ from each other in expansibility, but it has been observed that the dilatations of the same liquid are not proportionate to the increase of the temperature, and that they augment progressively when they approach the term at which they are reduced to vapour.*

In the experiments made by Ellicot, Smeaton,† General Roy,‡ La Place, and Lavoisier,§ on the dilatation of solid bodies by heat, there does not appear to be any relation between these dilatations and the capacity of bodies for heat, their hardness, or their other known properties, except, as it appears to me, with their fusibility; thus, in metals, platina dilates the least, and lead and zinc show this property in the highest degree; among glasses, those containing oxide of lead dilate much more than those which have not any.

* De Luc. Modif. de l'Atm. tom II. edit. in 8vo.

† Philos. Trans. 1788.

‡ Ibid. 1785.

§ Mém. recueillis par Seguin. tom II.

It may therefore be presumed, that it bears the same relation to the fusibility of solids, as it does to the vaporisation of liquids, and that the same solid substance does not experience uniform degrees of dilatation, at remote temperatures, but that on approaching to the term of liquefaction, the dilatations become proportionally greater.

This is a confirmation of the principle, that chemical causes exercise an influence before the effects they produce can be manifested (11).

105. These observations show, that heat dilates bodies in an unequal manner, with respect to each other. By the same temperatures, liquids experience an effect much greater than solids, and greatly inferior to elastic fluids; but in passing from one state to another, the dilatations participate in those belonging to the state into which the substances is passing; finally, the dilatations of volume do not correspond with the changes of temperature, when a body passes from a solid to a liquid state, or from this to the state of an elastic fluid: we must examine how these dissimilar appearances can be reconciled with the laws to which the action of caloric is submitted, and which have been just pointed out, and what correspondence can exist between the thermometric effects and the quantities of caloric which enter into combination.

106. In whatever state a substance is, its temperature always acquires an equilibrium with that of other bodies (90); so that caloric always tends

tends to attain correspondent proportions, according to the state of the substances among which it is distributed.

Pictet designates by the term *tension*, this property of caloric of distributing itself uniformly among different bodies, not in the ratio of their mechanical masses, but of their capacity in the state in which they are found, so as to produce an equilibrium of temperature between them; it may be compared to the effort of an elastic substance which acquires an equilibrium of elasticity with the other similar bodies which re-act upon it: nevertheless it must be distinguished from the expansive force of elastic fluids, although it is the principle of it: it acts indifferently in all bodies, whatsoever their state may be; but its effect is so much the greater as there is a greater distance between their temperatures; whence this conclusion may be drawn, *that caloric acts with so much the more energy between bodies, whose temperature is different, as its tension is greater.*

107. We have seen that the temperature was not raised during the liquefaction of ice, the same phenomenon takes place in the other solid bodies which pass to a liquid state, unless this effect is veiled by others: which shows that the elevation of temperature in solid bodies depends only on the resistance which the force of cohesion opposes to that of the caloric, and observation has already led us to consider these two forces as opposite. But when the distance, which the moleculæ, in conformity

conformity to their natural dispositions, would preserve between each other, according to the action they experience from caloric, is changed by compression, they abandon the caloric which is in excess in their new state, and their temperature is raised by all this excess, until they have yielded it to other bodies, or have been able to regain that state of dilatation, in which they would be in the equilibrium of temperature: hence the heat produced by compression and percussion.

The effects produced in liquids by caloric, are partly analogous to those observed in solids, and partly to those which take place in elastic fluids; but in these it appears that the pressure of the atmosphere is substituted for the reciprocal action of the moleculæ, and determines the proportion of caloric, according to the changes of temperature; on this pressure, also, depends the temperature a liquid is capable of acquiring before being reduced to a vapour. It will be proper, therefore, in the first place, to examine the correspondence which exists between the compression and the temperature of elastic fluids in order to distinguish its effects from those of the reciprocal action of the moleculæ, and with this view we must enquire what happens to elastic fluids when they are submitted to an equal pressure, but at different temperatures, and, when the pressure is different and the temperature remains the same.

108. Physiologists have long endeavoured to ascertain the dilatations experienced by the gases in

in consequence of an elevation of temperature, but from the diversity of the results of their experiments no correct opinion could be formed : a young chemist, Gay Lussac, whose talents have been particularly serviceable to me, removed all these uncertainties in a memoir which he read to the Institute,* an extract from which I insert.

Deluc, in comparing the heights found by the barometer, with those which had been measured geometrically, observed that towards the temperature of $16\frac{1}{4}^{\circ}$ which he calls fixed temperature, atmospheric air dilates $\frac{1}{277}$ of its volume for each degree.

Near the 15th degree, General Roy attributed a dilatation of $\frac{1}{172}$ to dry air and to humid air, a much greater dilatation. On this subject, Saussure observes, that this philosopher, by having introduced into his apparatus, either water or the vapour of water, has confounded two things which it was essential to have separated, namely, the conversion of water into elastic vapour, and the dilatation of air united to this vapour. According to experiments made from the 6th degree to the 22d, he fixed the dilatation at $\frac{1}{277}$ either of dry air, or of that which is more or less humid, but holding its water in perfect solution ; he also carefully guarded against the production of new vapours.

Priestley was the first who examined the dilatation of the other gases, but his experiments only

* Ann. de Chimie. Therm. An. X.

gave comparative dilatations very different from each other, and he does not himself seem to place much confidence in them.

Finally, Guyton and Prieur, have attributed to each gas a peculiar dilatation, increasing considerably on approaching the boiling point of water. For example, they found that azote gas from 0 to 20° dilated $\frac{1}{17}$ of its volume for each degree, from 20° to 40° $\frac{1}{16}$; from 40° to 60° $\frac{1}{15}$; and from 60° to 80° more than $\frac{1}{5}$; but this great increase of progression, and the difference of their results ought to be attributed principally to the water they left in their apparatus, and which as is known, acquires the elastic state the more easily as its temperature is raised. It must therefore have happened, that at 80°, the water being abundantly converted into vapour, expelled a great quantity of the air from their apparatus, which would not have been the case but for it, and that consequently they attributed to the remaining air a dilatation much too strong.

It was these great variations in the results of philosophers on the dilatation of the gases which determined Gay Lussac to enter on a new investigation. By avoiding in his apparatus all the causes of error he could foresee, particularly the presence of water, he found that atmospheric air, oxigen, hidrogen, azote, nitrous, ammoniacal, carbonic acid, sulphureous acid, and muriatic acid gases, and the vapour of sulphuric ether, dilated equally by the same degrees of heat, and that from

0 to 80° 100 parts of each of the permanent gases acquired an increase of 37.50 or $\frac{1}{27}$ of their volume for each degree.

This co-efficient $\frac{1}{27}$ appears to differ very little from the $\frac{1}{27}$ of Deluc; but Gay Lussac observes, that the difference of temperatures from which they arise, makes a very sensible difference between their results. He purposed also to show, that the co-efficients vary with the temperatures which produce them, and to determine the law of the variations.

He noticed, that on approaching the boiling point of ether, the condensations of its vapour were a little more rapid than those of the gases, which agrees with the greater dilatation experienced by liquids which approach ebullition, and with that manifested by some liquids when near congelation; but this effect is not perceptible some degrees above that at which it passes from the liquid state to that of elastic fluid.

Priestley, Guyton, and Prieur, found a very great dilatation in ammoniacal gas. If the ammoniacal gas proceeding from the decomposition of muriate of ammonia by common lime is received directly into the apparatus, there will also be found a very great dilatation; but in this case, on lowering the temperature, there will be observed, on the sides of the apparatus, a little liquid and some crystalline points, which are muriate or carbonate of ammonia; if the gas is kept over caustic pot-ash before it is introduced into

the apparatus, it will be found to dilate like the other gases, but then no liquid, or crystalline molecule will be seen in the receiver. This proves that, in investigations relative to the dilatation of the gases, those solids which are capable of taking the elastic state at the temperature to which they are exposed, should be as scrupulously avoided as liquids.

Since neither the greater or less solubility of the different gases, nor their greater or less density under the same pressure and at the same temperature, nor the peculiar nature of the gases and of the vapours, have any influence on their dilatation, it may be concluded, generally, that all the gases and all the vapours dilate equally by the same degrees of heat.

It is, therefore, confirmed by this, that all the gases, and atmospheric air which holds more or less water in solution, are equally dilatable. Saussure discovered this property in atmospheric air.

All the gases being equally dilatable by heat, and equally compressible, and these two properties being dependent on each other, the vapours, which follow the same laws of dilatation, must be also equally compressible; but this conclusion can only be true so long as the compressed vapours remain entirely in the elastic state, which requires that their temperature must be sufficiently raised to enable them to resist the pressure which tends to make them take the liquid state.

109. These experiments show that the reciprocal

cal action of the moleculæ has no sensible effect in the gases, but that under a uniform pressure, the dilatations produced by temperature are the same in all of them, and that all the liquids which have taken the gaseous state are subject to the same laws; so that their constitution depends only on the action of caloric, and on the resistance to compression. The elastic effort of a gas to occupy the volume which agrees with its temperature, increases in the same ratio in all the gases, and in all the vapours, if they can effectively receive this volume; and the comparative effect of caloric at different temperatures is proportionate to the tension which is produced in the elastic fluid: but if the volume can dilate freely, the tension remains the same, and all the effect of the caloric is limited to the dilatation of the volume.

It is only, therefore, because compression opposes dilatation that the temperature is raised, and one of these effects can make up for the other. Compression supplies the place of the reciprocal action of the moleculæ; with this difference, that this force is the same in all the gases, and that its effects are uniform and proportionate to its intensity, whereas the reciprocal action of the moleculæ varies in each substance.

110. Since compression supplies the place of the reciprocal action of the moleculæ, it is evident that by diminishing the compression, without changing

changing the temperature, the caloric must increase in proportion to the dilatation in volume.

If air is dilated by means of a pneumatic machine, an absorption of caloric, proportionate to the change produced in the volume of air, must take place, to enable it to preserve an equilibrium of temperature with the surrounding bodies. Nevertheless, the thermometer, immersed in this air, is lowered so slightly as does not appear to correspond with the effect which I have supposed, because the change indicated by the thermometer arises from the distribution of caloric between it and the substances with which it is in contact, according to their respective masses, and according to their capacities for caloric. When a thermometer is immersed in a liquid, particularly when the quantity of the liquid is considerable in comparison with it, the influence it possesses, in dividing its own temperature with that of the liquid, is so small that it is overlooked without causing any sensible error: but it is quite the reverse when the experiment is made with air; this, of which 100 cubic inches only weigh about 46 grains, is not only in contact with the thermometer which is many times its weight, but more especially with a considerable surface, part of which is metallic, and consequently well adapted to subtract readily the disengaged heat: only a very small part of its change of temperature, therefore, can act upon the thermometer, and its indication

cation is affected by all the difference arising from the quantity of air which absorbs the caloric, and of the bodies which furnish it. It is not, therefore, surprising, that the very great changes which take place in the proportions of caloric relatively to the air, should produce very slight ones in the temperature of the thermometer.

To the considerable change of temperature which takes place in air dilated by the pneumatic pump, is to be attributed the formation of the cloud to which such different explanations have been given, and which is so speedily re-dissolved by the air regaining the temperature of the surrounding bodies. If the reduction of the temperature was not much greater than is supposed, no sufficient cause could be assigned for this phenomenon.

What I have now advanced on dilatation, may be applied to the effects of compression; when, therefore, air is compressed, a quantity of caloric, proportionate to the diminution of volume, is eliminated. (*Note IV.*)

III. It may be objected, that when the air is compressed, the augmentation of its elasticity, shows that it retains a quantity of caloric, which, being itself in a state of compression, is the cause of this effort: that which proves that it is the same quantity of caloric which produces the equilibrium of temperature in both circumstances is, that if after having compressed the air it is again set at liberty, it produces a degree of cold corresponding

sponding with that of the heat which had been disengaged. If it had retained in compression a greater quantity of caloric than agreed with its reduction of volume at the given temperature, it would not regain the dimensions corresponding with the new compression; it would stop as soon as the compressed caloric should have acquired the equilibrium of the action of the adjacent bodies, and no diminution of temperature would take place in those bodies; it is not, therefore, by the action of compressed caloric that it endeavours to regain its primitive state. I cannot confirm this theory more strongly than by the opinion of La Place, who has been so obliging as to favour me with the annexed note. (*Note V.*)

The heat disengaged from solid bodies by those mechanical processes which approximate the moleculæ, and that expressed from elastic fluids by compression being an effect of the approximation of the moleculæ, (*Note VI.*), it will be seen why the friction, the agitation, and the compression of liquids, do not produce appreciable heat, since they are not sensibly compressible.

112.. Let us now return to ascertain what is the difference of the action of caloric on bodies, according to their state, and what are the phenomena produced by it in their passage from one state to the other.

There is this difference between solid bodies, liquids, and elastic fluids, that in the first the caloric is in a proportion correspondent with the state

state of dilatation produced by the temperature, and the reciprocal action of their moleculæ; when a body becomes liquid this must cease to produce its effect without an extraneous compression; but this compression keeps the moleculæ at such a distance that their reciprocal action can still take effect: the diminution of resistance permits the caloric to accumulate to a certain point without an increase of temperature, and in this diminution consists the cause why liquids can experience a greater dilatation than solids by the same elevations of temperature: finally, as the resistance continues to grow weaker, the caloric, by becoming preponderant, destroys it entirely, and accumulates until the elasticity communicated by it to the elastic fluid is in equilibrium with the compression, the latter having become the only obstacle which, by its intensity, causes a variation in the state of the new gas.

In this succession of phenomena there is an invariable correspondence between the quantities of caloric and the conditions to which a body is brought by its action; the temperature it acquires does not correspond with the accumulation of caloric, since a body may take a quantity greater than its change: dilatation is a more certain index; but it will be obvious, that it is not proportionate to the quantity of caloric, since it is incomparably greater in elastic fluids than in liquids, and in these than in solids, and that in its passage from one state to another, it participates in these

two

two conditions. (*Note VI.*). The caloric which becomes latent in the passage from a solid to a fluid state, and from a liquid to that of an elastic fluid, produces its effect in these opposite changes of state, in the same manner as that, which having raised the temperature, and become latent with respect to bodies of the same temperature, affects those which are at an inferior temperature.

A solid body may attain a temperature more elevated in proportion as it has less disposition to liquefy, or, as it opposes a greater force of cohesion to the action of caloric, and while it liquefies, the temperature is unchanged; all the caloric is employed in producing the liquid.

If the elevations of temperature in solid bodies are only dependent on the resistance experienced by the caloric from the reciprocal action of the moleculeæ, and, in elastic fluids, on the compression to which they are submitted, both causes act in liquids: we cannot in them, as in solids, increase the reciprocal action by compression, but we can diminish the effect, or cause it to disappear, as in elastic fluids.

113. The effects which, in the circumstances we have examined, are owing to the changes of bulk produced by a mechanical cause, or by the equilibrium of temperature, are likewise the same when they are produced by the action of affinity; but in this case they are frequently complicated with other results of affinity: it is only when the latter has but little energy, that the correspondence

dence of the quantity of caloric with the dimensions acquired by a substance, can be discovered in its integrity; such is evaporation.

If the cold produced by evaporation seems much greater with a very evaporable substance, such as ether, than that produced by the dilatation of an elastic fluid, it is because the effect is concentrated on the thermometer; at the bottom it is the same, or, there is no difference but in the quantity of the dilatation.

The congelation of water may even be produced at a pretty high temperature, as was done by Cavallo, by means of a small quantity of ether; if the vapour of the ether which is formed be collected by compression, the whole quantity of caloric which served to give it the elastic state will be disengaged, and, nevertheless, the thermometer will indicate but a small part of this effect; the reason of this is, because the caloric eliminated will be dispersed over the surface of the whole apparatus, and the thermometer, which is but a small part of it, will be but little affected; at the same time, if it is moistened with the liquid, the vapours will receive caloric directly from the thermometer itself. It is acknowledged, that in evaporation the vapour formed by solution in the air contains as much caloric as that produced by heat. Watt even concluded from his experiments, that the water held in solution by the air, contained more latent caloric than an equal volume of vapour; but this difference appears to me to be attributable

attributable to the inaccuracy inseparable from this kind of experiment. (*Note VII.*)

114. The observation of these phenomena proves, therefore, that the principles laid down, (103), are applicable to the changes of dimensions, produced in bodies by caloric, when affinity does not offer any obstacle, and when there is a uniform relation between the dimensions they acquire, according to the state of their reciprocal action, or of the compression substituted for this action, similar to that between their capacity for caloric, and the state they are in: with respect to the temperature, it corresponds with the obstacles opposed to the expansive action of caloric.

If the heat of a solid body is augmented progressively, it attains a degree at which the force of cohesion is so much weakened that it can no longer maintain its state, but takes that of a liquid or elastic fluid; and if, hitherto, some bodies have been refractory, it can only be attributed to the inadequacy of the means employed for accumulating caloric. Whenever heat has increased the distance between the moleculeæ of a substance so far that their mutual affinity yields to the action of caloric, the substance suddenly absorbs a great proportion; its moleculeæ combine without interruption, and immediately form a gas, which dilates more and more, preserving the same temperature, if this effect is not limited by the pressure of the atmosphere, which in that respect contributes to the results of chemical action, and by that

that of the gas itself which is formed : so that the caloric which raises the temperature above the equilibrium of the system of a body, produces that effect by the resistance opposed to its combination by the reciprocal affinity of the moleculæ and the pressure of the atmosphere. The caloric which becomes latent in these changes of state, re-appears during the return of an elastic fluid to a liquid state, and of the latter to a solid state. It is obvious, then, that the caloric which, in one circumstance, becomes latent, in another, produces thermometric effects, and that these are different according to the resistance it experiences, and vary in the different states of a substance, and in its passage from one state to another. (*Note VIII.*)

115. Bodies also differ by their property of communicating heat with greater or less facility, and of arriving more or less quickly at the equilibrium of temperature of the system in which they are placed, or by their conducting faculty ; but in considering this comparative faculty, in liquids and elastic fluids, the effects arising from the motion given to their particles by the alteration of the specific gravity, must be distinguished from those produced by the immediate communication, as I shall show more particularly.

CHAP. II.

Of the different States of Caloric.

116. THE results deduced from immediate experiment, or from accurate reasoning on the action of caloric, are true, independently of the ideas which may be formed on the nature of caloric, and whether it may be considered as a force only known by its effects, or as a substance which exercises the properties belonging to it.

Yet it is important to theory, to show the relation of the properties of caloric with each other, and the influence they may have in complicated phenomena, in order to ascertain the differences which may distinguish this power from all those which enter into chemical action: this will not be the only advantage obtained, if it can be proved that the action of caloric is analogous to that of a substance which enters into combination with others, but there will be this further advantage, that its effects will be made to depend on a cause common to all chemical phenomena, considering it nevertheless as a fluid eminently elastic, and capable of an indefinite condensation. The only question is, whether the explanations given on this hypothesis are exactly applicable to the phenomena; this is the only method capable of being applied to an object which escapes the weights and

and measures, which can alone uncontestedly certify the existence of a body; and if these explanations correspond in a satisfactory manner, we shall be authorised to consider it as a substance which has the property of entering into combination with others, passing by such discussions as are useless in the explanation of chemical phenomena, and, which not being capable of being judged by experiment, are indeterminable.

117. In classing the effects of caloric, *sensible caloric* and *latent caloric*; *specific caloric* and *absolute caloric*; *free caloric* and *combined caloric*, are distinguished from each other: we must inquire what there is of reality in the modifications of caloric, which have led to these distinctions, and examine if they are all deducible from the properties of chemical combination.

The effects produced by caloric when it affects our senses, or when it causes a variation of temperature, and a dilatation of bodies, are attributed to free caloric. These have been represented as a sponge, the spaces of which absorbed the caloric, which tended to occupy them in endeavouring to place them in an equilibrium by a property common to all fluids; nevertheless, some celebrated philosophers have believed it to be the action of an affinity tending to condense the caloric, but they have distinguished it from the affinity which produces combinations, under the name of physical affinity, or affinity of adherence, or of cohesion, and have attributed the union of caloric (*? free*)

(? free) to this first affinity, and that of combined caloric to the second.*

This manner of considering caloric does not appear to me to be conformable to the indications of experience. We may be easily convinced, that the caloric which produces sensible effects, does not correspond with the interstices which may be supposed to be between the moleculæ of different bodies : the capacity for caloric of an equal weight of water, that is to say, the quantity of caloric it can abandon in passing from one given degree of temperature to another, compared to that of alcohol, is in the relation of 1000 to 678 ; † the dilatations produced by the same quantity of caloric in the volume of a gas, are incomparably greater than those experienced by liquids, and more especially by solids, and there is no correspondence between the dilatations and the quantities of caloric absorbed.

To produce the same effect, caloric combines with different substances in different proportions, in the ratio of its affinity for them, and not of the interstices they may contain.

118. The difference between the caloric which they consider as free, and that which they call combined, does not warrant the attributing their states to two distinct affinities, for we have seen in the preceding chapter, that caloric only raises

* Pictet, Essais de Phys. p. 13.

† Mém. sur la Chaleur.

the temperature of a body because it meets with an obstacle which prevents it from giving to it the dimensions necessary to maintain a tension equal to that of the adjoining bodies: the only difference, therefore, between the caloric which they have considered as combined; and that which they have called by the name of free caloric, consists in this, that one produces a saturation, whose equilibrium does not change in given circumstances, and that the other is in a different degree of tension, on account of the forces opposed to a dilatation proportionate to its quantity, and that it is consequently more disposed to enter into other combinations which are not at the same point of saturation; if this obstacle is removed, the excess of saturation will disappear, and the caloric considered as free will become latent.

Caloric, as soon as it produces any effect on a body which experiences no change in its state of combination, augments its bulk; it increases the distance of its molecule, and subdues their reciprocal affinity, an effort which is immense, compared with the mechanical forces which can be attributed to particles, extremely subtle and of great mobility, and which offers no analogy, except with that powerful force which produces chemical combinations. In the union which it contracts, it follows the same laws as we have noticed in that of acids, and which are generally found in every species of combination; with this difference, that its affinity unites it with all the

bodies which are within a system exposed to the same temperature, that is to say, which attain to the same degree of saturation; while an acid can only establish its equilibrium of saturation with the alkalis, and finds, with respect to other substances, either in the force of cohesion, or in the elasticity which it must overcome, and in those which belong to itself, a resistance which it cannot surmount: we shall be convinced of this by comparing the effects.

Just as it requires different quantities of the same acids to produce the same degree of saturation with different alkaline bases, so it requires different quantities of caloric to produce the same degree of saturation in different bodies, or, which is the same thing, to raise them from any given temperature to another.

Specific caloric, or the comparative quantity of caloric which can produce the same effect, the same degree of saturation with different bodies, corresponds, therefore, with the quantity of any acid which is necessary to produce the same degree of saturation, for example, neutralization, with different bases, or with the quantity of different acids required to produce this effect with the same base: but all the acidity necessary to produce neutralization can be ascertained, while the quantities of caloric can only be compared by the uniform effects they produce on a substance which serves as an object of comparison.

An acid becomes latent in a combination, but its

its acidity reappears whenever another substance divides the action exercised by it on the base, with which it had been combined without opposition.

Thus, sensible caloric is that which passes from one combination to another which is not at the same degree of saturation: it establishes an equilibrium of saturation, and the proportions necessary for this effect, in the same manner as with an acid, depend on the affinities for caloric, and on the ponderable quantity of the base; they each become latent, until a superior force obliges them to pass into another combination, or rather to submit to another division. The compound acquires the qualities which depend on the proportions of its composition, and the opposing forces are saturated according to the element which governs: but as alkalinity is the force opposed to an acid, so is the force of cohesion to caloric.

119. Latent caloric is, therefore, that which, in the same circumstances, preserves its state of combination; but, in other circumstances, it may, in its turn, become sensible caloric: now, specific caloric being the quantity of caloric which can become sensible, by quitting a combination in a determinate space of the thermometric scale, compared to that which abandons another combination, in the same circumstances, it differs from latent caloric only in the comparative saturation produced by one and the other.

By producing liquidity in solid bodies, caloric

enables their particles to exercise their mutual affinity: it is thus that solid bodies, insoluble by water, become, by fusion, capable of forming a vitreous substance, which is homogeneous and which can assume the crystalline form determined by its particles, when the temperature is lowered, that is say, when its action is diminished, as in solutions in water.

In the same manner as a liquid can dissolve a greater quantity of two saline substances than of one alone, because the mutual action of the two substances concurs with that which the liquid exercises, so caloric liquefies two substances, whose particles exercise a mutual affinity, with greater facility than it acts on insulated bodies; as is seen in alloys, which are more fusible than the metals of which they are formed; and as is observed in vitrifications, in which non-vitrifiable earths serve as fluxes to other earths which alone would resist the degree of heat which produces the vitrification.

When, therefore, caloric causes the liquefaction of solid bodies, either immediately, or by the intermediate action of a liquid, it acts like the solvents, and, in this point of view, may be assimilated with them: like them, it produces reciprocal liquefaction by diminishing the effect of the affinity of the particles of each body, by an analogous effect of affinity. The more it is superabundant in a combination, the more its properties predominate, and the more elastic does the substance.

stance become: then its action becomes prejudicial to the combination of this substance with another which does not acquire the same elasticity, and it may be considered as a solvent which operates the separation of the two substances.

120. Before it destroys the force of cohesion, or separates a substance by the volatility it communicates to it, its proportion must have arrived at a certain term, then it accumulates rapidly (114), and as soon as its action yields to that of the forces opposed to it, the bodies have acquired the same proportions of it.

If we direct our attention to the liquefaction produced by a solvent, we shall discover similar effects.

The water begins by combining with a solid, until its force of cohesion be sufficiently weakened; then the solid dissolves at once, it takes the liquid state directly without passing through intermediate states, and is soluble in every proportion by another liquid, if its specific gravity causes no obstacle; but the more abundant the water is, the less does the superfluity adhere to the combination; if by evaporation, or by the action of another substance, the water is separated from the solution, the solid body is restored to its former state, and retains the same quantity of water as it had at the moment it passed into the liquid state.

If this conformity between the properties of caloric and those of a substance which enters into combination

combination be not considered as a rigorous proof of its substantial existence, it will not be denied that the hypothesis of its existence is free from inconvenience, with the advantage of not introducing into the explanations of the phenomena any principles but such as are general and uniform.

121. Although the specific caloric of a substance bears a constant relation with the dilatations it experiences, at different temperatures, and although it is probable that there is also a correspondence between the dilatations of different bodies and their specific caloric, we are still ignorant what this is in the greater number of circumstances: it is only seen that the dilatations of elastic fluids indicate less specific caloric than those of liquids, and these less than the dilatations of solids; thus, the condensation of a metal is accompanied with a disengagement of caloric much greater than a similar condensation in the same ponderable quantity of a gas.

It appears to me, therefore, that the more the condensation of a substance augments, the greater is the quantity of caloric separated from it by a similar change of bulk; or, in other words, that the caloric is in a more condensed state, the more its quantity is diminished, which is in conformity with the increasing action of the affinities by a decrease of the proportions.

All the quantity of caloric which can form specific caloric, appears therefore to have a constant relation

relation with the state of the expansion of a substance, but not with its absolute caloric; for example, the specific caloric of the vapour of water has no relation with that of the water: when the vapour is reduced into liquid, the caloric disengaged is that which brought it to the gaseous state, and all that which belongs to the water has no influence on the phenomenon; it is the same with the caloric which the water parts with in its conversion into ice, and which forms the specific caloric of the water; but it is probable that the ice can and does retain a much greater quantity of caloric than that disengaged between the state of vapour and that of congelation; since chemical action increases, as the proportion of an element diminishes, it follows therefore that it must be much more condensed than that which constitutes vapour.

There is this difference between solid substances and liquids and gaseous fluids, on which I shall insist elsewhere, that when the latter enter into a powerful combination, they experience a much greater condensation. This condensation must be incomparably more considerable in the caloric than in the other substances, which derive their elasticity from it.

If the caloric was not more condensed in bodies in proportion as their molecular approximate, or rather, if that which is the nearest to each molecule, was not in a greater state of condensation than that which is more remote, the specific calorics

rica would be proportionate to the dilatations: it may be conceived, therefore, how its quantity must always correspond with the volume, or with the specific gravity of the same body, if its tension remains the same; for, having the property of combining with all bodies, it abandons that whose molecule approximate, because it may be said to be expelled, by that which surrounds the molecule in the state of condensation effected by their action, to produce a dilatation in other bodies, by which means it still retains the state of condensation agreeing with the action which it experiences.

122. Hitherto I have only considered caloric in the effects it produces on bodies, and consequently in those circumstances in which it exercises an action on them: I have shown that this action is perfectly analogous to that of a substance which combines; but the elasticity of which it is possessed in an eminent degree, gives it a property which distinguishes it from the combinations in which this force does not contribute to the effects, and of which we may form an idea by considering what passes in a weak combination of an elastic substance, for example, in a solution of carbonic acid in water; more especially since it is the principle of this property in all the substances which possess it.

If, after having saturated water with carbonic acid at a certain pressure of the atmosphere, this pressure is diminished, part of the carbonic acid escapes

escapes and resumes the elastic state; this disengagement of gas takes place in the same way if its elasticity is augmented by raising the temperature: the more energetic these two causes of separation may be, the greater will be the quantity of carbonic acid which returns to the elastic state.

The same phenomenon takes place in caloric combined with a substance: if the circumstances which are necessary to enable a heated body to attain a certain degree of temperature, be weakened, part of the caloric escapes, and preserves its elastic state until it loses it by combining with a body: it is then *radiant caloric*, whose properties I shall now examine.

123. The radiant caloric, discovered by Mariotte, was submitted to experiment by Lambert, under the name of obscure heat; Scheele distinguished it more particularly by the name of *radiant heat*.* Saussure afterwards occupied himself with it;† but it is Citizen Pictet‡ to whom we are more especially indebted for making known its properties by some very delicate experiments.

Scheele observed that radiant caloric is reflected by metallic mirrors, which do not receive any heat by its action, but which are warmed, if their surface is blackened; that it is absorbed by glass

* *Traité Chim. de l'Air et du Feu.* p. 118.

† *Voyages dans les Alpes.* tom iv. édit. in 8vo.

‡ *Essais de Phys.*

which

which transmits only the light, and that the latter may be afterwards reflected by a metallic mirror without heat; that air receives no heat from it, while it takes it from a heated body; that for this reason the breath of a person placed in a current of radiant caloric is visible in winter, although a temperature, much less sensible, renders it invisible in summer; that from the same cause a current of air is not affected by radiant heat, so that a light preserves its direction in it, and it does not produce that undulation on shadows excited by a hot body with which it is in contact.

Radiant caloric escapes, therefore, from bodies heated and placed in the atmosphere without producing light, or else it is blended with the light; in the latter case it is reflected by metallic mirrors with the light, but it is absorbed by glass lenses and mirrors which only reflect or transmit the light, until the glass is sufficiently heated to emit radiant caloric from itself.

When, therefore, Pictet examined the variations of a thermometer exposed, in a receiver, to the influence of a taper, it was not the radiant caloric emitted directly by the taper which produced the variations, but that proceeding from the heated glass, and his results must be adopted with this modification.

Thus, radiant caloric is absorbed, after reflections more or less multiplied, by the surfaces of the surrounding bodies, more rapidly by some, for example, by black bodies; more slowly by white

white bodies : the polish of the surfaces also contributes to its reflection, and it seems to be entirely reflected by metallic bodies ; it finishes by wholly combining, if the surrounding bodies arrive at a perfect equilibrium, and it is only by its combinations that it produces any effect on them.

If, on the contrary, the equilibrium is broken, a part of the combined caloric of the hottest bodies is disengaged under the form of radiant caloric, and tends to combine with the bodies of an inferior temperature : one consequence of this effect, as has been shown by Pictet, is that a cold body placed in the focus of a concave metallic mirror, produces a reduction in a thermometer in the focus of another concave mirror placed opposite to the first, as if cold itself could be reflected. He proves that the two effects only differ in the direction in which the emanation of the caloric moves, and according to the degree of the tension of the bodies ; so that according to the circumstances, one effect becomes the inverse of the other. This learned philosopher examined the differences offered by radiant caloric, in *vacuo*, in the vapour of water, and in the gas of sulphuric ether. He found that there were none, except in the intensity of this property, which is a little stronger in *vacuo* than in the vapour of water, and in this than in ethereal gas. It may, therefore, be considered as a general property of the gases

gases to give a free passage to radiant caloric, and it appears that they possess this property in proportion to their expansion; nevertheless, it must not be considered as absolute.

On the contrary, liquids do not seem to permit the transmission of radiant caloric, or at least it is so rapidly absorbed, that this effect may be considered as null, and the tension of the caloric, which is in the direct ratio of the elevation of temperature, and inverse to that of the capacity for caloric, must only be considered in liquids and more particularly in solids, with respect to each other, as a tendency to the equilibrium of saturation.

124. From the property possessed by air, according to the observation of Scheele, as well as by the other gases, of not combining with radiant caloric, it results that whenever combustion, or a disengagement of caloric from any other cause, takes place in the air, only one part is employed; immediately, in raising its temperature, so that a thermometer exposed to the influence of radiant caloric, may sometimes lead to error respecting the temperature of the air, since it can absorb the radiant caloric which does not combine with the air.

It is only to radiant caloric that a strict application of the denomination of free caloric can be made; but in using it thus, it must not be overlooked, that no real effect is produced by it on bodies,

bodies, except when it enters into combination with them, and that its existence is not yet proved except in elastic fluids.

CHAP. III.

Of the Action of Light, and of the Electric Fluid.

125. Light contributes greatly to chemical phenomena, it is the cause of many combinations, and is produced by means of many others: it is, therefore, one of the agents whose characteristic properties it is proper to be acquainted with; but it is always necessary to distinguish the consequences to which observation and analogy lead, with respect to those beings which cannot be submitted to weight and measure, from the determinations which are founded on this invariable base.

When bodies change their volume they take or they abandon caloric, according as their new dimensions are more contracted or more extended: if these changes are made with rapidity they are accompanied, not only by heat, but also by light; thus, iron becomes hot and luminous by a brisk percussion; the oxygenated muriate of pot-ash detonates with sulphur and other easily combustible

tible bodies by simple percussion, and much light is disengaged; a mixture of iron and sulphur suitably moistened deprives oxygen gas of its elasticity, and, according as the absorption is more or less rapid, and more or less abundant, the heat disengaged is either scarcely perceptible, but continued for a length of time, or it is brisker, or in the end combustion takes place accompanied with much light, and the results whether slowly or quickly obtained are the same.

It would be useless to accumulate facts so well known, for the purpose of deducing the conclusions arising from them, and which are, in addition to those already indicated, 1st. that whenever the volume of a body diminishes, the caloric which exceeds that quantity which it must contain, passes into combination with the adjoining bodies, producing in them the dilatation required by its introduction, according to the quantity and capacity of these bodies: 2d. that if the phenomenon takes place with a gas, part of the caloric takes the state of radiant caloric, which afterwards enters into combination either with liquid or solid bodies: 3d. that, in the last case, if the quantity of caloric eliminated is considerable, or rather, if the elimination is rapid, more or less light is disengaged: 4th. that combinations produce, in this respect, effects analogous to those of mechanical pressure; but these effects are generally much more considerable, because the power of affinity is much more energetic than the mechanical powers which

which are at our disposal, or than we are capable of observing: nevertheless, since the action of the two elements of a combination on caloric may vary considerably, according to that which either of them could exercise in an insulated state, and according to their reciprocal affinity, the results of the combination may be very different, and may not correspond with the energy which produces it.

126. According to this theory which is adopted by the greatest number of chemists, light may be fixed in bodies, and it then resumes the properties of combined caloric; in fact, coloured bodies, and more especially if they are black, grow hot by absorbing it; white bodies heat much less, because they reflect it; glasses transmit the greatest part of it, but they absorb a small quantity, and, in consequence, acquire a little heat: when it is collected in the focus of a lens, or reflected in that of a concave mirror, it produces all the effects of accumulated caloric in another mode, with this difference, that the bodies experience greater effect as they are more opaque or more coloured.

This difference in the mode of communication between caloric and light is shown in an experiment indicated by Scheele: "On exposing," says he, "to the rays of the sun, two equal thermometers, the one filled with spirit of wine coloured of a deep red, and the other filled with spirit of wine uncoloured, the red liquor will rise much sooner than the white; but if the two ther-

" thermometers are placed in warm water, their
" liquors will rise at the same time."

In the same manner, radiant caloric becomes combined caloric when it is fixed, but it is distinguishable from light, because it is absorbed with greater facility, and by bodies which transmit light; glasses and transparent liquids which give no passage to radiant caloric, allow that of light, (123). It appears, therefore, that this distinction must be admitted between radiant caloric and light; that the first possesses less of the qualities of eminent elasticity, or that it is endowed with less velocity: this difference depends only on the circumstances of their emission, since one can take the nature of the other, and since both can, in the end, perform the functions of caloric, when they are obedient to the action of bodies; but neither can produce any effect, except when they enter into combination.

127. If observation shows that radiant caloric and light fulfil the functions of caloric, by their fixation in bodies which experience no change in their combination, and by losing the properties which characterise them; if, in consequence, we are warranted in considering them as one and the same substance, which differs only by the state in which it is found, there are nevertheless some chemical combinations which seem to experience different effects from light and heat, and which seem to lead us to consider them as distinct substances: thus, when nitric acid is exposed to light, oxygen gas

gas is disengaged, and nitrous gas is formed; heat, on the contrary, disengages nitrous gas from nitrous acid: oxygenated muriatic acid abandons its oxygen by the action of light, and it can, by that of heat, be distilled without decomposition: the effects produced in other combinations appear to be similar, for example, when a solution of Prussiate of pot-ash, in which a little acid has been mixed, is exposed to the action of light, it is rapidly decomposed; one part of the Prussic acid is disengaged because it resumes the elastic state; another part is precipitated in Prussiate of iron: when this solution is submitted to ebullition it undergoes the same decomposition; but if it receives no higher temperature than it would have taken from the action of light, it experiences no change.

We must examine what are the circumstances which can produce these effects, which, in some cases, announce only a difference in the energy of the action of light and heat, and which, at other times, seem to prove that there is a greater distance between them: to this end it will be proper to follow some of these cases in detail, comparing the two agents which produce them.

128. We are indebted to the celebrated Count Rumford for some very interesting experiments on the effects of solar light, as well as on those of heat.*

* Philos. Papers, vol. i.

I shall divide these experiments into two classes; those in which, with a solution of gold, he produced a purple colour, and with a solution of silver a yellow brown, and those in which he obtained a reduction of these metals.

He impregnated white silk, linen and cotton cloth, and magnesia alba, with a solution of gold; on exposing these substances to the light of the sun, or to the heat of a taper, they took a beautiful purple colour, but in the dark no change was produced. When they were not humid, heat and light caused little alteration in them, but by moistening them, the effect took place.

With solution of silver the same substances took a yellow brown shade, but in the dark, and without heat, they acquired no colour.

I have made some experiments on muriate of silver which may elucidate these results. Scheele observed that muriate of silver, covered with water, and exposed to light, abandoned the muriatic acid, so that the supernatant water formed, with the solution of silver, a new precipitate of muriate; but he supposed that the silver was blackened because the light had brought it nearer to the metallic state by having given phlogiston to it. To explain the effects of light, in a manner more conformable to observation,* I had presumed that the muriate of silver suffered its oxygen to escape when it was exposed to light, like

* Journ. de Phys. 1786.

the oxygenated muriatic acid; that it took its black colour by approaching the metallic state from that cause, and that it abandoned the muriatic acid with which it could not remain in combination in this state. I have submitted this old conjecture to experiment.

Muriate of silver covered with water, and then exposed to the sun's rays for several days, at first only disengaged some bubbles which appeared to be owing to the air adhering to the muriate of silver, and driven off by the water; for, when the first effect had ceased no more gas was disengaged, although the quantity of muriate of silver was considerable, and it was frequently agitated for the purpose of renewing the surface exposed to the rays of light: the water which had become acid, reddened paper tinged with turnsole without destroying its colour, it therefore did not contain oxygenated muriatic acid. Saturated with soda, it yielded muriate of soda by evaporation. The muriate blackened by the light was entirely dissolved in ammonia, like that which had preserved its whiteness.

I was not, therefore, warranted in supposing that in this case the oxygen was disposed to resume the elastic state, and to abandon the metal, by the action of light.

I exposed muriate of silver blackened by light to heat, in a small glass retort placed on sand; it entered into fusion and combined with the glass: oxygen was not disengaged, but muriatic acid.

Muriate of silver which had not experienced the action of the light was submitted to a less degree of heat, and it was remarked that it became blackened before it entered into fusion, and that, at the same time, a little muriatic acid was disengaged, but no oxygen. It appears, therefore, that light only occasions the separation of a portion of the muriatic acid which is combined in the muriate of silver, and that heat alone can produce the same effect.

Muriate of silver, left in a dark place, but exposed to a current of air, blackened quickly, as if it had been submitted to the action of light: the air therefore favours the disengagement of that part of the muriatic acid which must be separated to enable the muriate of silver to acquire a black colour, and this separation may be the effect of very different causes.

There is a probability that the muriate of gold experiences the same effect as the muriate of silver, and that light, as well as heat, separates a part of the acid, but that the intervention of water favours this effect, since the dry substances did not take the purple colour. The colour taken by the combinations of gold and silver are the same as those of the oxides of these metals when they predominate: this explains the remark of Rumford, that the colours obtained from them resemble those of the enamels into which these oxides enter.

129. I proceed to the experiments in which Rumford,

Rumford, guided by those previously made by Mrs. Fulham, obtained the reduction of the two metals. He exposed to the light of the sun, a flask containing pieces of charcoal and a solution of gold; in a short time the gold was completely reduced: the solution of silver experienced a similar reduction: the metals form a brilliant coat on the glass to which they attach themselves, or are deposited in pellicles or in crystals on the surface of the charcoal. Similar flasks were enclosed in cylinders of tin, and exposed to the heat of boiling water, with the same result, so that the heat of the ebullition of water produces a similar effect to that of the rays of the sun; this is contrary to the opinion Rumford had formed of the high temperature which light was capable of communicating to the moleculæ on which it exercised its action, as he has observed himself with that candour which characterises him.

I repeated these experiments on the solution of silver, having adapted a tube to the flask for the purpose of examining the gas which might be disengaged, and I obtained, in both circumstances, a mixture of nitrous gas and carbonic acid: I also exposed nitric acid, into which I had put pieces of charcoal, to the action of light, and to that of boiling water, and I obtained, in the same manner, in both experiments, nitrous gas and carbonic acid.

130. Rumford submitted the solution of muriate of gold in ether to the action of light, and observed

gases to give a free passage to radiant caloric, and it appears that they possess this property in proportion to their expansion; nevertheless, it must not be considered as absolute.

On the contrary, liquids do not seem to permit the transmission of radiant caloric, or at least it is so rapidly absorbed, that this effect may be considered as null, and the tension of the caloric, which is in the direct ratio of the elevation of temperature, and inverse to that of the capacity for caloric, must only be considered in liquids and more particularly in solids, with respect to each other, as a tendency to the equilibrium of saturation.

124. From the property possessed by air, according to the observation of Scheele, as well as by the other gasses, of not combining with radiant caloric, it results that whenever combustion, or a disengagement of caloric from any other cause, takes place in the air, only one part is employed; immediately, in raising its temperature, so that a thermometer exposed to the influence of radiant caloric, may sometimes lead to error respecting the temperature of the air, since it can absorb the radiant caloric which does not combine with the air.

It is only to radiant caloric that a strict application of the denomination of free caloric can be made; but in using it thus, it must not be overlooked, that no real effect is produced by it on bodies,

bodies, except when it enters into combination with them, and that its existence is not yet proved except in elastic fluids.

CHAP. III.

Of the Action of Light, and of the Electric Fluid.

125. Light contributes greatly to chemical phenomena, it is the cause of many combinations, and is produced by means of many others: it is, therefore, one of the agents whose characteristic properties it is proper to be acquainted with; but it is always necessary to distinguish the consequences to which observation and analogy lead, with respect to those beings which cannot be submitted to weight and measure, from the determinations which are founded on this invariable base.

When bodies change their volume they take or they abandon caloric, according as their new dimensions are more contracted or more extended: if these changes are made with rapidity they are accompanied, not only by heat, but also by light; thus, iron becomes hot and luminous by a brisk percussion; the oxygenated muriate of pot-ash detonates with sulphur and other easily combustible

acids are retained by an alkali, which puts them into a state in which they can receive the action of a high temperature. Let us enquire on what the difference found on this occasion depends: its explanation may be applied to all similar cases.

Rumford observed that light might elevate the temperature of the moleculæ on which it acted, although that of the substance, of which the moleculæ are a part, appeared to receive but little heat: the circumstance which hinders the common temperature from being the measure of the effect produced on some parts, is the same which causes a thermometer to indicate but a small part of the change experienced by a small quantity of air, compared to that of the mass with which it shares its temperature (110). But this effect has much less intensity than the first considerations of it led to believe.

In the oxygenated muriatic acid the light can only be reduced to a state of combination, by the action of oxigen; it is to it that its action is limited: it therefore produces on it alone the effects of a high temperature, so that it resumes its elastic state, as it would have done by an elevation of temperature.

If heat is communicated to the liquid by a heated body, it acts equally on all the liquid, the temperature of which, by being raised, renders the water and the muriatic acid volatile; so that the liquid comes over by distillation, without any difference being produced which can cause the separation.

separation of the oxygen; but if the muriatic acid is retained by an alkaline base, its temperature may be raised so high that the disengagement of oxygen can take place.

When, therefore, light produces the disengagement of oxygen gas from oxygenated muriatic acid; from nitric acid; from a plant which vegetates; it must be concluded that it enters into combination, that it supplies the quantity of caloric wanting to the gas which is disengaged, and that, in raising its temperature, it increases its elasticity; and if radiant caloric or heat does not produce the same effect, it is because, in the given circumstances, it cannot form a similar combination, or occasion its effects.

132. These observations appear to me to confirm the identity of the substance of light with that of caloric; but they indisputably confirm the identity of their effects, with some differences, which only arise from the conditions in which they act.

Colours have no influence on the action of caloric, but they render bodies more or less fit to fix the light and to change it into caloric, so that a white body, placed even in the focus of a burning glass, experiences effects much less considerable than a black body, because it is only that part of the light which enters into combination that can produce chemical effects in a substance.

Light is sometimes fixed by one element of a combination rather than by another, so that, in that case, it acts on it in an insulated manner, while

while caloric would have been uniformly combined with all the elements. These effects of the solar light can only be compared to those of a temperature but little elevated; but if the rays are concentrated they act with the greatest power that can possibly be obtained from caloric; to judge of it from its effects, radiant heat appears to be in an intermediate state between light and combined caloric.

Such are the results of observation: some philosophers have been of opinion that light was a substance distinct from heat; Deluc has insisted strongly on their difference; but Saussure seems to me to have proved the weakness of the grounds on which he endeavoured to establish it.* A celebrated philosopher has recently relied on some phenomena, which are still obscure, and of little weight, to distinguish the calorific rays from the luminous: admitting that this distinction was realized, it would occasion no change in the explanation of the chemical phenomena, which is founded on the effects of light, such as it comes to us.

133. But light is separable into different rays, and we suppose that caloric is an identical substance; this is caused by our comprehending under the name of caloric, the object to which all the properties of caloric belong, in the same manner as many of the effects of the atmospheric air are explained without a necessity for attending to the component parts of it. It is therefore possible, it is even probable, that caloric contains se-

* Voy. ans les Alpes. Tom IV: Edit. in 8vo.

veral substances really different, and that it is a genus to which several species belong; but hitherto little difference has been observed in the chemical action of the rays of light: nevertheless, Scheele noticed that the violet ray had more action on muriate of silver than the other rays.

Sennebier examined the effect of the prismatic rays on the same substance, and ascertained their difference by that of the time required by each to bring it to the same shade. In fifteen seconds the violet ray produced the same effect as that of the red ray in twenty minutes; the other rays were intermediate: * there is doubtless much knowledge still to be acquired on the physical nature of colours, and the theory of caloric, as well as on most other subjects.

134. If the disengagement of light only differs from the elimination of caloric by the circumstances of its emission, we need not be surprised that it should be produced by very different causes; its most usual source is the combination of oxygen with some inflammable substance; but other combinations, or even the compression of a substance may produce it; it is sufficient that, under certain conditions, a change in the proportion of caloric in a body, or of the system of a body, should be made. (*Note IX.*)

The calorimeter indicates all the caloric disengaged; but the combustion which takes place in

* *Mém. Physico-Chim.* tom III.

the atmosphere permits all that part which takes the state of light to escape, and all that which is disengaged in radiant caloric to be dispersed to a distance, until substances, either liquid or solid, are enabled to bring the one and the other into a state of combination.

Light appears to be retained by some substances which make but little change in its elastic state, and which permit it to be easily restored by a slight cause, as is observed in atmospheric air, which adheres to some bodies from which it is separated with great facility. It is probably in this manner that some bodies become luminous in the dark, after having been exposed to a vivid light; but this effect must not be confounded with that of other substances which experience a true combustion. (*Note X.*)

135. Besides the effects which constitute the electric phenomena, the action of the electric fluid produces changes in the chemical properties of bodies, and thus favours the formation or decomposition of many combinations; hence it must be reckoned among the chemical agents.

If the chemical effects of the action of electricity are compared with those of caloric, the greatest analogy will be found between them.

The electric spark inflames the mixture of oxygen gas and hydrogen gas, from which the formation of water takes place in the same manner as by an elevation of temperature: both of them favour evaporation and increase the specific levity
of

of the elastic fluids;* both decompose ammonia; and, by means of a metal, the water held in solution by carbonic acid: they equally favour the combination of azote and oxigen, or the production of nitric acid; the combustion of turnsole by the air,† as well as that of inflammable liquors; the disengagement of hidrogen from ether, oils and alcohol; the oxidation of metals, or, according to their intensity, the disengagement of the oxigen of the oxides. ‡

Nevertheless, the electric fluid does not always act like caloric, which passes into combination by immediate communication with a substance, but its action is at first condensed on some of the moleculeæ of a substance, and then it produces effects analogous to those we have noticed with respect to light, (131); the only difference is, that its effects are much more considerable than those of the ordinary light of the sun; thus, while the latter disengages the oxigen from common water and nitric acid, the electric fluid can disengage it not only from nitric acid, but even from sulphuric acid; it can decompose water entirely when shocks are passed through this liquid, although in other circumstances, whose differences I shall endeavour to explain, it effects its production.

* Van Marum, 1^{re} Suite des Exp. p. 210.

† Cavendish. Philos. Trans. 1785.

‡ Descrip. d'une très grande machine électriq. p. 168.

It must not be concluded from the identity of these effects, that the agents are the same; on the contrary, observation seems to prove that there is an essential difference between them: very little change of temperature is observed from the action of electricity: when the metals enter into combustion it is to it alone that the heat they acquire should be attributed; for if an incombustible metal, such as gold, silver or platina, is submitted to a strong shock, we do not perceive that it can have taken a heat capable of effecting its fusion, though this would have happened with no other difference but that of a greater shock, which only produces liquefaction by an elevation of temperature. The heat produced in this case seems to me to be an effect of the compression exercised by those parts which are most dilated, upon the others: no conclusion opposite to this opinion can be drawn even if we succeed in bringing a metal to a red heat without the contact of oxygen, since percussion can produce this effect. (*Note XI.*)

The action of the electric fluid causes such a dilatation in that part of the bodies on which it acts, that it seems to reduce them into gas with greater facility than that of caloric which liquefies them, at least if we judge from the effect produced by it on the metals, and which has been so carefully described by Van Marum.

This dilatation seems to me to be calculated to explain the analogy of chemical effects: in either circumstance

circumstance the force of cohesion is diminished by the distance introduced between the molecular, and, by this, the combinations, to which this obstacle was opposed, are effectuated.

136. Lately, electric effects, which at first appeared to have a particular character, and of which the cause has been indicated under the name of *galvanism*, have exercised the penetration of philosophers and chemists: although the series of phenomena to which this species of observation has given birth, are worthy of forming a distinct branch of philosophy, their connection with many chemical phenomena induces me to extract from the celebrated Volta, a sketch of the luminous theory he has given *.

All the phenomena of the pile, or of the electromotive apparatus, are deduced by Volta's theory, from a generative property, principally possessed by the metals.

The metals exercise a mutual action with respect to the electric state natural to them: in an equilibrium of electricity while insulated, they share that which belongs to them, unequally, as soon as they come into contact; some surcharge themselves with the electric fluid at the expense of others, but in an unequal manner; hence this effect is greater between some metals than between others: in this respect a series of metals may be formed, and the two extreme terms of the series

* Ann. de Chim. Frimaire An. X.

are zinc, which takes the electricity from all the others, and gold or silver, which yield it to all the others. The intermediate metals take it from those which occupy inferior places in the series, and give it to those which fill superior places.

This property is not confined to the metals, charcoal may be compared with those which are the most disposed to give the electric fluid by contact, and crystallized oxide of manganese yields a greater quantity than even gold or silver.

While the metals remain insulated in their contact, this mutual action only produces a first effect; but if a communication is established, on one side with a reservoir of electricity, and on the other with conducting bodies, the metal which has yielded electric fluid to another, for example, the silver which has given it to the zinc, receives it from the reservoir, and resigns it continually to the zinc, which transmits it to the conducting bodies; thus a continued current is established: a liquid conducting substance, such as water, receives therefore the electric fluid which passes from the silver to the zinc, but if it communicates with a plate of silver, which is itself in contact with a plate of zinc, and which exercises a similar mutual action, the effect of the two latter plates is added to that of the two former, from this there results a greater tension in the electricity which is disengaged; hence, all the properties of the pile, whose action augments in the arithmetical ratio of the number of its elements:

but

but if the pile is insulated, this action of its elements accumulates the electric fluid in the upper part, at the expense of the lower, so that the superior half, being surcharged with electric fluid, is in a positive state, and the inferior in a negative state, while the centre of these forces, being counterbalanced, remains in the natural state.

Nevertheless the electric current formed by a pile, which is not composed of numerous elements, does not possess a tension which produces a sensible effect on electrometers; but the tension of the electricity proceeding from this pile, may be augmented by means of a condenser, and the augmentation it receives by increasing its elements may be ascertained by means of an electrometer, whose graduation has been formed on the comparative effects of sparks produced by an electrophorus: it was thus that Volta was enabled to measure the action of each element of the pile, and the compound action of all the elements.

He also proves, by the rapidity with which a large reservoir is charged by the most instantaneous contact of the pile, taking the same tension of electricity as the pile, that the quantity of electric fluid which circulates in a given time, is much greater than that which it could receive, even from a vast machine, in the same interval of time.

This property of the pile, of giving motion to a great quantity of electric fluid, renders its

effects analogous to those of a Leyden phial, the action of which is maintained without interruption, and elucidates all the phenomena which it was, before, natural to attribute to a chemical action of the substances employed; an action which seems to perpetuate the electric effects.

We must here distinguish the action of the conductors from the chemical decompositions which take place. The current is more rapid, and its effects are more sensible, in proportion as the liquids interposed between the elements of the pile are better conductors, without having recourse to the intervention of their chemical properties: Volta has proved that it is only from this property that muriate of soda, muriate of ammonia, nitric acid, &c. augment the effects of the pile so as to produce a shock, without increasing the tension of the electric fluid.

Priestley had noticed before that the *caustic* alkali and muriatic acid were incapable of rendering the electric spark visible, whence he concluded that, *they must be much better conductors of electricity than water and the other fluid substances**. Morgan made the same observation on all the mineral acids †.

The dimensions of the surfaces of the elements of the pile, and of the wet cloths that are interposed, produce a peculiar effect, of which Volta

* Exp. et obs. sur diff. espèces d'acid. Vol. I. p. 321.

† Philos. Trans. 1785.

confesses

confesses he is not able to give more than a probable explanation. An electromotive apparatus so composed of large plates, produces a great effect on metals, whose combustion it causes with facility, as has been shown by Hatchett, Thenard, Fourcroy, and Vauquelin*, and nevertheless the tension of the electric fluid is not greater than that of an ordinary pile, neither is that of the shocks which it occasions.

Volta conjectures that the cause of this difference is, that the human body being a worse conductor than the metals, opposes a resistance to the electric current which moves with a weak tension, and that this superior resistance prevents the augmentation of the quantity of the electric fluid, in the ratio which could be furnished by the large plates, while the metallic wires are capable of receiving and being acted upon by their influence†.

With respect to the chemical effects which take place, they seem to be the consequences of the electric action, and we have already observed that electricity favours many combinations, and many decompositions, in the same manner as an elevation of temperature, and that to produce this effect it is sufficient that the electricity tends to separate the moleculæ of the bodies which it affects, because by that means it destroys the obstacle of

* Journ. de l'Ecole Polyt. tom IV.

† Bibl. Britan. Vol. XIX.

the force of cohesion : caloric itself only favours combinations and decompositions by being a force opposed to that of cohesion.

The action by which two substances in contact make a different division of the electric fluid, is not only peculiar to the metals and to some analogous solid substances, but also belongs, as has been shown by Volta, to liquids; so that the mutual action of two different liquids may produce an electric current, provided that an interposed metal serves at the same time as a conductor: a third liquid may even replace the metal.

138. In the mean time several philosophers have continued to collect interesting facts on the nature and on the action of this electricity: Wollaston *, among others, has shown that a metallic wire, extremely thin, and covered with a coating of glass, is even capable, by its uncoated point, of decomposing water, with an electrical machine of moderate power, thus he has proved that if the dimensions of the passage of the electricity is contracted, it is sufficient to produce this effect, although in itself, it is not very considerable. Van Marum confirmed clearly the identity of the current of electric fluid, whether produced by the pile, or by the electrical machine †.

139. Nevertheless there is still a difference between the manner in which water is decomposed

* Bibl. Brit. Vol. XVIII.

† Ann. de Chim. Frim. An. X.

by the common electricity and by that of the pile : the first, in all the experiments yet known, separates the two elements of the water, and disengages them blended in one single elastic fluid ; but by the action of the pile, the hidrogen escapes from the metallic wire which communicates with the silver, that is to say, with that end of the pile which has negative electricity, and the oxigen by that which communicates with the zinc, or with the positive end of the pile. If we do not admit properties, irreconcileable with those best established in natural philosophy, it would seem, that this insulated disengagement of each of the elements of water must be explained, on the one hand, by the property possessed by water, as well as by all the combinations known, of receiving different proportions of the substances which compose it, when the forces which produce the composition are counteracted by other forces ; and, on the other hand, by the property which may be supposed to be in positive electricity of favouring the disengagement of oxigen, and in negative electricity of being, on the contrary, more favourable to the disengagement of hidrogen ; but that circumspection which is requisite in philosophical enquiries, compels us to wait until experiment has decided on a subject which still retains some obscurity, and it is probable that it will not be long before the question will be finally determined.

By

By these discoveries, which form an epocha in the history of sciences, chemistry has acquired an agent whose energy may perhaps be carried to a degree, which, as yet, can scarcely be imagined, and which will furnish the means of producing, in the formation and decomposition of chemical combinations, effects, unforeseen, and superior, in some circumstances, to those which it is possible to obtain by the action of caloric.

CHAP. IV.

Of Caloric considered with relation to Combinations.

189. THAT which has been advanced in the first chapter concerns the effect of caloric on insulated bodies alone; but the results, which we have collected from observation, are not applicable to the changes which take place when the same substances enter into combination with others, and especially, if at the same, their constitution experiences any alteration.

Whenever an energetic combination is formed, a heat, more or less considerable, is found to accompany the act of combination; thus, when the alkalis

alkalis are combined with the acids, heat is always disengaged: this effect takes place in a combination which produces the liquefaction of a solid, such as lime, and even in that which causes the disengagement of an elastic substance, as carbonic acid: so that this alone shows how deceitful it is to consider that as the principle of a general application, which is only established on the consideration of one kind of these phenomena.

In the solution of salts and in the liquefaction of ice, cold is produced, or caloric is absorbed; nevertheless there is an act of combination, and the effects are varied by different circumstances: it is only when several causes act that their effects can be counterbalanced, and the result they then give is the excess of some over the others.

As this subject has exercised the talents of many philosophers, I shall examine it fully, and shall endeavour to determine the circumstances which cause the results to vary, comparing the effects observed in the insulated bodies with those which take place in solutions, and in combinations, according to the energy of the affinity which produces them, and, afterwards, with those which are accompanied by a considerable change of the constitution.

140. When a liquid, water for instance, passes to a solid state, a disengagement of caloric takes place, as also when from the vaporous state it passes into that of a liquid, only, in the latter circumstance,

circumstance, it is much more considerable: observation shows, that when bodies pass from a liquid state to a solid state, they experience a condensation; and if water and some other substances augment in volume, it can only be attributed to the arrangement of the moleculæ which crystallize, whence it follows that when bodies pass from the liquid state to the solid state an approximation of the moleculæ is effected, by the predominance of the reciprocal affinity, analogous to that which takes place when vapours pass to the liquid state, but which is much less considerable, because the volumes are in that case much less compressible.

This approximation of the moleculæ, arising from the preponderance of the reciprocal affinity, is accompanied by an elimination of caloric, the proportion of which is always determined by the actual volume of a body.

When a combination is formed, an approximation of the moleculæ also takes place, which is so much the greater, compared with the actual state of the body, as the combination is more energetic; but at the same time there are changes in its state, so that a solid substance may become liquid by the influence of that with which it combines: let us examine, in the first place, what happens when the action of the combination is weak, such as in ordinary solutions.

141. When two liquids act there is always a condensation of volume, and, at the same time, a disen-

disengagement of caloric, as is observed in the union of liquid acids and alkalis, and also in the union of alcohol and water: but if a liquid dissolves a solid, two causes act, both on the volume and on the caloric; the body which passes from the solid to the liquid state, by the action of the solvent, experiences a modification, similar to that which would have arose from its liquefaction by caloric, and opposite to that which is observed when it passes from the liquid to the solid state, that is to say, it acquires an augmentation of bulk, and, by that means, absorbs and renders latent a certain quantity of caloric; but on the other hand, combination produces a contrary effect, it diminishes the bulk and disengages caloric: the result depends on which of these effects predominates, so that an acid, in dissolving ice, may yield heat, if that which would result from its union with the same quantity of water, is superior to that which the ice would absorb by its reduction to water; but it will produce a contrary effect if the absorption of caloric by the ice is greater than the disengagement of it produced by the solution of the same quantity of water: whence it follows that the effect must vary by the concentration of the acid, that is to say, by the quantity of water which it holds in solution, and which has already produced its effect; by the proportion of the ice on which it acts; and, by the action it can exercise on the force of cohesion at certain temperatures. These effects, noticed by Wilks,
and

and particularly by Cavendish, have been exhibited very clearly by the authors of the *Mémoire* on Heat. "If the mixture of an acid with a given quantity of water produces heat, by mixing this acid with the same quantity of ice, it will produce heat or cold, according as the heat which results from its mixture with the water is more or less considerable than that which is necessary to melt the ice; we may, therefore, suppose a degree of concentration for the acid, which we will call K, and which on being added to an infinitely small part of ice produces neither heat nor cold. This being admitted the greatest cold that the mixture of acid and ice can produce, is that, at which the acid concentrated to the point K, ceases to dissolve the ice: the *maximum* of cold may be determined without producing it, by observing, at the lowest degrees of cold, the law which exists between the degrees of the thermometer and the corresponding degrees of concentration at which the acid ceases to dissolve the ice."

142. The same effects are observed in the solution of salts by water, or in that of ice which they produce.

An observation which renders the contrast very remarkable is due to Lowitz. He has shown* that red pot-ash and soda, which produce a ~~heat~~ heat on being dissolved in water, yield,

Journal de Chim. tom XXII.

on the contrary, a remarkable cold, when, being in a crystalline state, their solution in water is effected, and much greater when they are made to act on ice or snow.

These alkalis only differ then in respect of caloric in this, that in crystallization they abandon a part and experience a contraction of their volume; but they regain this caloric by solution in water, and undergo a dilatation of volume equal to the preceding contraction; consequently the quantity of water they retain in their crystallization, made or occasioned a loss of caloric equivalent to all that would have produced the caloric, which would have been disengaged if, after having dried them strongly, they had been dissolved in water: in fact, it results from the observations of Watson,* and of Vauquelin,† that there is a dilatation of volume by the solution of all the neutral salts in water. When these salts dissolve ice, the effect is compounded of that which they would have produced on the same quantity of water, and of that of the caloric which this quantity would have absorbed to pass from the state of ice to the liquid state.

The degree of cold which proceeds from the mutual solution of salts and of ice would therefore be much more considerable than that arising from the liquefaction of ice by the acids which pro-

* Philos. Trans. 1773.

† Ann. de Chim. tom XIII.

duce heat with water, if they could dissolve an equal quantity; but this effect is limited because the force of cohesion of the salts is augmented much more rapidly by cold than that of the acids, and may be said to suspend their action, as will be seen hereafter.

Nevertheless, some salts retain the superiority, and Lowitz has shown that muriate of lime is the most proper substance to produce a great degree of cold, and it is by the proportions of this muriate which he has pointed out, that Fourcroy and Vauquelin congealed ammonia and ether,* and that Pepys solidified 56 pounds of mercury.†

It is, therefore, to their solubility at a low temperature, that the salts principally owe the differences they offer in causing cold by their action; a confirmation of this is, that sulphate of soda scarcely produces any cold with ice, because, as has been noticed by Blagden,‡ as soon as the water which holds it in solution is lowered a little below the freezing point, it crystallizes and separates; but if it is dissolved by nitric acid, provided it is in a crystallized state, it produces a very great degree of cold, as has been proved by Walker,§ and for this purpose it may supply the place of snow: phosphate of soda and sulphate of magnesia have the same property.

* Ann. de Chim. tom XXIX.

† Bibl. Brit. No. 140.

‡ Philos. Trans. 1788.

§ Nicholson's Journ. Sept. 1801.

The mutual action of salts is so weak, that it causes but little change in their respective volumes; it, however, diminishes their force of cohesion, and by that means augments their solubility: from this it results that mixture must increase the frigorific property of salts, and this has been proved by Blagden and Walker; but if a salt is, of itself, very soluble, the addition of another salt does not sensibly augment its action, as Walker has observed in respect of muriate of lime.

The greater part of the salts which are deprived of their water of crystallization, cause the thermometer to rise, by solution in water, so that the effect of the condensation arising from the combination is, in this case, superior to that of the passage from the solid to the liquid state; but this property of desiccated salts is not general.: Walker remarked that muriate of ammonia, although evaporated to desiccation, produced, nevertheless, a considerable cold; it is probable that this combination, and all those which are in the same situation, experience a considerable dilatation by solution in water.

143. There are other phenomena resembling those I have now analysed, and on which Blagden has made some very interesting observations. This learned philosopher has shown that the salts lower the freezing point of water, each in the simple ratio of the quantity which is held in solution; and that the effect which they can produce
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on ice is proportionate to the degree of temperature to which they can lower the water without suffering it to congeal; so that the ice which they can liquefy at any temperature is equal to the quantity of water which they can prevent from congealing at the same degree.

He remarked that one salt added to the solution of another, lowered the freezing point of the solution nearly as much as it would have produced by its sole action, and that the same effect took place if a third salt was added to the preceding, so that a judgment may be formed, from the quantity of the salts which can be held in solution by a proportion of water, and from the temperature at which they can maintain themselves without precipitation, of the quantity of ice which they can dissolve, and of the degree of cold which they can produce.

He shows that the temperature to which salts can lower the thermometer is limited by this circumstance, so that if there is a great proportion of salt, the effect is prolonged, the cold is maintained at a uniform degree, and the liquefaction of the ice continues until it has absorbed successively all the caloric necessary to reduce it into water, and all that which the salt would have required for its solution in the water.

The experiments of Vauquelin* also elucidate the effect produced by the mixture of salts: he

* Ann. de Chim. tom XIII.

has shown that when muriate of soda is dissolved in a saturated solution of another salt, it frequently happens that no cold is produced; that, on the contrary, there is frequently a disengagement of caloric; and that it is always disengaged when there is a precipitation of the salt previously dissolved. These observations are explained by the slight condensation that the mutual action of the salts must necessarily produce in their volume, although their solubility is augmented for the reasons which shall be hereafter given.

With respect to the caloric, the effect which is owing to the concentration of the volume diminishes that of the dilatation which would have been produced if the salts had been dissolved separately, and where there is a deposition of a part of the salts, to this first quantity must be added all the caloric disengaged from the salt, which, by its separation, abstracts the water, as in an ordinary crystallization; but if the salts act on ice, their augmentation of solubility predominates in the result.

It will be seen nevertheless from this, why Blagden found that the addition of a salt did not cause all the reduction in the freezing point of water, which it could have produced when separate; all the effect of the condensation of volume arising from the reciprocal action must be deducted from it: the liquefaction of ice by a mixture of salts is also diminished in the same proportion, and thus all the phenomena correspond.

The

The counterbalance of effects produced by the solution and by the changes of volume which depend on the chemical action, and on the passage from a solid to a liquid state, does not take place in the passage from the liquid state to that of elastic fluid, because the mutual action of the gases does not occasion any change in the volume which they occupy, (109); for which reason the preceding observations are inapplicable to evaporation.

145. In the greater number of the facts which I have pointed out, the effect of the liquefaction is superior to that produced by the combination; but this is not the case when the latter has much energy, then the action of the combination covers and renders imperceptible that arising from the liquefaction: thus, desiccated alkalis produce heat by solution in water; but this heat is much more considerable, if they combine with an acid which exercises a much more powerful action than water, this effect varies according to the degree of concentration of the acid, if it has already disengaged much caloric by its combination with water, it eliminates less when it combines with the alkali, because the condensation it has experienced with the water diminishes that which it undergoes by its combination with the alkali, and that which the water has experienced is, in part, re-established, since, by the combination of the acid with the alkali, it obtains a restitution of its volume which is equivalent to the diminution of the action exercised on it.

146. When

146. When the combinations which are formed are accompanied by a great change of constitution, the phenomena become more complicated; there is no longer any connection perceived between the changes of volume and the temperatures produced: thus, when an alkaline carbonate is dissolved in an acid, a little concentrated, carbonic acid is disengaged, yet at the same time heat is produced; in the solution of copper by nitric acid, there is a liquefaction of copper, a disengagement of a great quantity of nitrous gas, and, notwithstanding, a great production of heat; in the detonation of nitrate of pot-ash with charcoal, a development of much heat is accompanied by the formation of a great quantity of gas.

It must be recollectcd, 1st. That the gases, by the same changes of temperature, receive an augmentation of volume much more considerable than that acquired by liquids, and particularly by solids, (112): 2d. That when the elastic fluids are retained in a combination, their tendency to elasticity is an effort which continues to act, and which produces its effect as soon as the force that retained it is sufficiently weakened.

When, therefore, a gaseous substance can be formed, either because this substance experiences a resistance inferior to that which retained it, or because it is the product of a combination which is formed, it must escape in gas, while, at the same time, the quantity of caloric which it requires for this would produce but a slight change in the

bulk of the substance which remains solid or liquid.

Hence it will be seen how the carbonic acid, disengaged in the first instance, could occupy a volume much greater than before, notwithstanding, it absorbed but a small part of the caloric eliminated by the combination.

Nevertheless, this effect of the action of an acid on a carbonate is not general; but its exceptions are calculated to show the distinction between the effects produced by combination and those which are owing to the formation of elastic fluids, as has been done by Lavoisier.*

The solution of carbonate of ammonia, which contains a great proportion of carbonic acid, yielded a little cold with nitric acid; but by abstracting a part of the carbonic acid from the carbonate, by means of lime, there was a production of heat which was increased in proportion as the quantity of the carbonic acid carried off by the lime was greater.

In the second example, the oxygen which is combined with the copper, perhaps, sustained all the loss of the caloric necessary to enable the nitrous gas to take the elastic state, and thus all the heat arising from the action of the nitric acid on the oxide might be disengaged.

To explain the third case, it must be again observed that the circumstance which reduced the

* Mém. de L'Acad. 1777.

oxygen

oxigen to the solid state had changed, and that it must only be compared with that which would have happened if it had been found in the elastic state: it is evident, therefore, that the combination was in reality accompanied by a great reduction of volume.

147. Nevertheless, it must not be concluded that the caloric disengaged bears a constant relation with the bulk produced, even in those combinations which remain in a solid or liquid state; this conclusion is only strictly applicable to insulated substances which do not undergo combination: the difference of the action of the elements, which enter into combination, on caloric, and the changes which result from their reciprocal action, and which vary with the temperatures, cause considerable alterations in the results; thus oxigen retains the greatest part of its caloric in nitric acid, and abandons much more in other combinations in which it experiences less condensation: but observation teaches us, that although there is not a relation between the quantities, there is nevertheless always an elimination of caloric, when a substance passes from a weaker combination to a stronger, unless this effect is disguised by that of the change of volume which accompanies the change of state; thus the oxigen which combines with nitrous gas abandons a little of its caloric; it abandons more by being united with water, and a still greater quantity by combining with an alkali. Among all the combinations yet

known, there are only superoxygenated muriatic acid, and some metallic oxides which can be conjectured to be exceptions.

148. From all which precedes, it results, that the immediate effect of all combination is an elimination of caloric; that this effect may be disguised in weak combinations, by the changes of bulk occasioned by the passage from the solid to the liquid state, or from the liquid to that of elastic fluid; but that when they are energetic, the effect of combination, with respect to caloric, always overcomes that of the accidental dilatation of volume; and that nevertheless there is not, in combinations, the correspondence between the changes of dimensions and the eliminations of caloric, which is observed in insulated substances: hence it would be an error to establish it as a general principle, that dilatation is always accompanied with reduction of temperature, and it would be another to pretend that combination constantly produces heat. These effects may sometimes balance each other, or the excess of one above the other may produce the result.

149. The caloric disengaged during a combination is a quantity as invariable as that which is determined by the dimensions of an insulated body, but the dimensions produced, compared with those which preceded, cannot be ascertained by means of it; other conditions, arising either from the affinity of the elements of the combination, or from their reciprocal action, limit the proportion

proportion in which it can enter into it, and the state of condensation in which it can exist in it. It is with this modification of the relation of caloric to the dimensions, that the principles laid down, (103), can be applied to insulated bodies, and to substances which enter into combination.

These two species of phenomena have not only been frequently confounded, but also the specific caloric, or the quantity of combined caloric which a body is capable of taking or abandoning by passing from one given temperature to another, and the whole of the combined caloric, or the absolute caloric. I shall endeavour to ascertain the state of our knowledge on this subject.

Crawford laid it down as a principle, that the capacity for caloric was unchanged while a body preserved its state; from whence he concluded, that the capacity of a body for caloric was proportionate to its absolute caloric; and he endeavoured to determine the one by the other.

150. The gases and vapours, as we have seen, all follow the same law of dilatation; they all take, at the same temperature, a quantity of caloric proportionate to the dimensions which are produced by the pressure; thus it may be said, that their capacity for caloric is proportionate to their volume; but it is not known what are their differences of capacity with respect to each other, or what quantity of caloric each gas requires to attain the same degree of dilatation; it is still unknown

known whether these capacities are changed by the elevations of temperature, although they preserve the same relation to each other: but if it is considered that oxygen gas has only a weak capacity for caloric, and yet that certain combinations show that it contains a great proportion, it will be found probable that the capacities of the gases for caloric experience great variations at remote temperatures: with respect to liquids, and particularly water, the experiments of Deluc and of Crawford seem to prove that they remain the same during the thermometric interval which separates congelation and ebullition; in that space, the action of the moleculæ on caloric, and their reciprocal action, do not appear to experience a change sufficiently considerable to cause any sensible effect on their capacities, or at least if there is a variation in the term which approaches congelation, and more especially in that which approaches to ebullition, it is because the passage from one state to another, which has an influence on the dilatations, can probably also affect the capacity for caloric; this constancy in the specific caloric may be adopted as the explanation of these phenomena; but that which has been observed in this part of the thermometric scale is not applicable to the different temperatures which solid bodies can receive.

These take the solid state, not because their moleculæ touch, since there is a probability that they are still at very great distances in respect of their bulk;

bulk ; but because the action they exercise on the caloric, and by which they condense it, is in equilibrium with their reciprocal action : the more their particles approximate, the more the caloric which remains is condensed, and the stronger is the affinity which retains it.

This supposition, which is founded on the attributes of affinity, seems to me to be realised by the observations I have offered on the accumulation of caloric, when its action becomes more powerful than that of the force of cohesion, or of compression, and on the distinction which must be made between the specific caloric of ice, of water, and of the vapour of water which is formed under different pressures at the heat of ebullition, or which is exposed to higher degrees of temperatures, (120, 121).

It should result from this, that the specific caloric of solid bodies augments in proportion as their volumes diminish ; but, on the other hand, by equal elevations of temperature, the dimensions increase in greater proportions, and the resistance of the cohesion diminishes : experience has not yet shown whether these effects counterbalance each other, or if one is greater than the other. I conclude, therefore, that there is no known relation between the capacities of solid bodies for caloric, at different temperatures, although in the small extent of the thermometric scale, between the freezing and boiling points of water, these changes are so small as to be imperceptible, since
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the dilatations which these degr es of heat produce are themselves extremely small.

151. Crawford has given a great latitude to the principles he at first adopted on the constancy of the capacity for caloric, while the state of the bodies was unchanged. From the variations of capacity which he observed in a combination, notwithstanding the changes of state which its elements might have experienced, he has deduced the absorption or disengagement of caloric which took place: thus, he explained the phenomena of respiration by the capacity for caloric of the carbonic acid which formed, compared with that of oxygen gas.

I shall not notice here the inaccuracies arising from the method he employed to determine the capacity of gaseous substances for caloric, and of those which form combinations.

The authors of the Memoir on Heat have sought to discover what the absolute quantity of caloric in water is, by determining experimentally its specific caloric, as well as that of several substances with which they combined it, and also the quantity of heat disengaged in these combinations; but these experiments gave very different valuations for the absolute caloric of water, and appeared to them to destroy the hypothesis, that the specific caloric is proportionate to it; nevertheless, they admit that a small error in the determination of the specific caloric would be sufficient to introduce this difference, because it can only be

be a very small quantity in comparison with the absolute caloric; but they made another experiment, the result of which has nothing doubtful. They mixed one part of nitrate of pot-ash with eight parts of water; it is known, that in the solution of pot-ash cold is produced, and, consequently, the specific caloric of the solution should be greater than that of the two substances when separate; now the specific caloric of the solution which depends solely on the water, and without taking into the account that which belongs to the nitrate of pot-ash, and the increase which has been spoken of, should be 0.88889, valuing the specific caloric of water at 1.0000; yet the experiment only gave 0.81670 for the specific caloric of the solution.

The nitrate of pot-ash which in this experiment diminished the specific caloric of the water, contains nevertheless more than 0.30 of oxygen, which retains nearly all the caloric it had in the gaseous state, and, according to Crawford, oxygen gas contains almost five times as much specific caloric as water: it would not be difficult to accumulate similar instances, which demonstrate that no conclusion can be formed from the specific caloric of the separate elements of a combination, with respect to that of the combination, nor from the specific caloric of a substance, of the total quantity it may contain; although all these quantities may be the same under the same conditions.

Since

Since the proportion of caloric not only causes variations in the force of cohesion, but, by changing the dimensions unequally, introduces a force which modifies the chemical action of the different substances, it will now be proper to consider the properties derived from it.

SECTION

SECTION IV.

*Of the Effect of Expansion and Condensation in
Elastic Fluids.*

CHAP. I.

*Of the Characteristic Properties of Elastic
Fluids.*

152. SUBSTANCES are differently affected by caloric, so that some only experience a dilatation, and preserve the solid state at the highest degree of heat that can be obtained, unless some affinity concurs with the action of caloric; others, on the contrary, retain the elastic state at the greatest reduction of temperature, and under the strongest pressures known, and the energy of affinity alone, more powerful than these means, is capable of destroying their elasticity.

Some substances keep a medium between these extremes; at a given temperature and pressure, they remain in a liquid state; another temperature, or another pressure, reduces them to the state of elastic fluid: they are then distinguished from the gases by the name of vapours.

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These different properties depend on the greater or less reciprocal affinity of the moleculæ of a substance, and on its correspondence with the affinity which these moleculæ have for caloric; but as these two effects cannot be distinguished, we are confined to the examination of their result, considering it as a force, which is variable in the different substances according to their nature, and in each substance according to the circumstances in which it is found.

Thus, having examined solidity as a force which favours combinations, or which is opposed to them, I shall, in this chapter, consider elasticity as another force, whose effects it is necessary to appreciate. I shall examine it in the different circumstances of chemical action, independently of the causes to which a substance is indebted for this disposition, and of the laws which the caloric obeys in this action.

153. Carbonic acid can only combine with water in a small proportion at a température a little raised; this is not because the water has no tendency to unite with a greater quantity, for, on diminishing the force of the elasticity by compression, this solution may be augmented indefinitely: the same effect is also produced by lowering the temperature, but in that case it is limited by the force of cohesion which the water acquires at the degree of congelation, and which, by vanquishing its affinity for carbonic acid, obliges it to abandon it: and it is probable that the preparatory

ratory force of crystallization, which is manifested by a dilatation, some degrees above the term of congelation, produces an analogous effect on the solution of gaseous substances in water, so that it is not at the freezing point itself that the water can dissolve the greatest quantity of these substances, but at some degrees above it: finally, an opposite result will be obtained, by diminishing the pressure, or by raising the temperature, if the process takes place on a combination of carbonic acid with water saturated at a low temperature, or by a strong pressure.

As these effects may be observed in all the combinations of gaseous substances, with the differences depending on the intensity of the combination, it results, 1st. That elasticity is to be considered as a force opposed to the combinations of any substance possessed of it, with liquid or solid substances, or with those having a different degree of elasticity; 2d. That this force is increased by the accumulation of caloric, which, by that means, causes variations in the combinations which may be formed at different temperatures: it follows therefore from this that the action which two liquid substances exercise on an elastic fluid may be compared by the quantities which an equal weight of each of them can overcome.

154. When a liquid substance, which tends to a combination with carbonic acid cannot any longer overcome its elasticity at a given temperature

190 EXPANSION AND CONDENSATION

ture and pressure, the tendency to combination with this acid which it retains is equal to that of all the substances in the same situation: but the term, at which the action of a substance stops, which becomes solid, is sometimes very distant from that which it could attain, by causing an incipient diminution of the effects of the elasticity by a preliminary solution; thus carbonate of lime may be dissolved by water impregnated with carbonic acid.

As the carbonate of lime is still very distant from the term at which the tendency of its base to combine with carbonic acid would be exhausted, at the ordinary temperature of the atmosphere, it is only by exposing it to a high degree of heat, that the carbonic acid acquires a sufficient disposition to elasticity to be enabled to begin its disengagement; and as the proportion of the carbonic acid is diminished, the heat must be augmented to continue the disengagement, it is not until the disposition to elasticity has become superior to all the action which the lime can exercise, that it can be entirely deprived of this acid.

The great quantity of carbonic acid with which the alkaline bases can enter into combination, by overcoming its elasticity, proves what an enormous force they can exercise. It is obvious therefore that elasticity counteracts the affinities which tend to produce a combination, as the force of cohesion acts in a contrary sense: it is to be regarded

regarded as an effort which may be compressed; but it may increase to a point at which it overcomes the affinity which produces combinations and thus it is the cause of separations when it becomes predominant; the one produces precipitation, and the other volatilization, and these two opposite forces, which we shall presently compare, may contribute equally to the combinations which are formed in many circumstances, and which have been attributed to the elective affinities.

We have noticed that the force of cohesion becomes active before it realizes the solid state (9); elasticity shows still more clearly the force it exercises before the production of the elastic fluid takes place, since the elastic tension of a liquid is increased by the causes which augment this force, in proportion as it approaches the term at which it can produce its effect.

155. If an acid, whose natural state is liquidity, is brought into action with one naturally elastic, such as the carbonic acid, but which is combined with an alkaline base which compresses its elasticity, the tendency of this base to combination divides its action between the two acids, in the ratio of their capacity for saturation, and of their quantity, so that the saturation of the carbonic acid is less in proportion as the force opposed to it is greater; if therefore it was combined in a considerable quantity with the alkaline base, for instance, to the point of neutralization, it, in part,

part, obeys the elastic force, which relatively, has become greater than the saturation, and is volatilized: it then no longer opposes the same mass to the other acid; by this its relative force is diminished: thus, although the affinity, or capacity for saturation of the opposed acid may be much weaker, it will be able to disengage the carbonic acid, if the quantity is enough to saturate the base; but if the alkaline base holds only a small proportion of carbonic acid, another acid cannot drive this off until it shall be in a sufficient quantity, so that at the commencement of the mixture there will be no effervescence; this is, in fact, what is observed when an acid is added by successive portions to the solution of an alkali which is combined with only a small proportion of carbonic acid. The effervescence is not manifested until the quantity of acid added has become sufficiently great. The effect becomes more rapid and more complete, if the force of elasticity is increased by heat.

It is to this effect of elasticity that the decompositions produced by the most fixed acids, in the combinations composed of a fixed base and a volatile acid, are to be attributed, particularly if the elasticity is augmented by heat, independently of the capacities for saturation; then the force which depends on the proportions of a substance gradually disappears, and the action of the elasticity increases relatively, or, effectively, if the temperature is raised; it is thus that sulphuric acid, by means

means of heat, decomposes the muriates, and nitrates with a fixed base: I distilled a mixture of oxalic acid and muriate of soda, and the liquor which passed contained much muriatic acid: nevertheless when there is no great difference in the volatility of the two acids, the stronger affinity of the one may overcome the effect of elasticity alone; thus having repeated the same experiment with acetic acid, it passed alone in the distillation.

156. If one base is volatile, and, at a temperature a little elevated, it divides the action on an elastic acid, with a fixed base, the heat which augments the elasticity of the base and of the volatile acid will determine their separation and their combination, as the force of cohesion determines the separation of the combinations to which it belongs.

These separations which are decided by the volatility and by the fixity, are produced more easily and more completely, when the substances in action, are all in a neutral state, because it is in that state that the relative action of acids and alkalis is the strongest: by applying what I have said on the reciprocal decompositions by the force of cohesion (*Chap. IV. Sect. II.*) to all the observations which have been made on those which take place by the elevation of temperature, it will be found that they can be explained completely by this second cause, analogous to the first: a table of respective volatility would equally show

the combinations which could be formed, by the action of heat, in the mixture of different substances, except in those cases in which the dispositions of two substances, in a competition of combination, are but little different, and in which affinity may then produce a complex combination in preference to a binary one, as I have remarked with respect to combinations which differ little in their solubility.

Since the relation of the force of cohesion with the elasticity is varied by the different degrees of heat, it frequently happens that after having formed a combination by the preponderance of the first, an opposite one is produced by augmenting the latter; thus when carbonate of ammonia is mixed with muriate of lime in a liquid state, carbonate of lime, which is insoluble, is formed and precipitates; but if muriate of ammonia and carbonate of lime are exposed to the action of heat, it is carbonate of ammonia which separates and is sublimed.

When, therefore, a liquid acts on a gaseous substance, the latter combines until the resistance of the elasticity is in equilibrium with the action of the liquid, so that by varying the circumstances which augment or diminish the mutual action of these substances, either by the quantity of the liquid, the compression of the gas, or by the temperature, the equilibrium between the action of the liquid and that of the gaseous substance is changed: whence it may be concluded that, when, it

it is intended to combine a (? gaseous) substance with a liquid, the temperature must be lowered, and, the action which is required for the combination of a liquid with a solid substance reversed.

Nevertheless the action of caloric may favour the combination of an elastic substance by diminishing the force of cohesion; this takes place particularly with solid bodies, but then a degree of heat superior to that which produces this effect may again destroy the combination which is formed; thus mercury requires a certain degree of heat to combine with oxygen, which regains its elastic state by a more elevated degree.

A proof that heat acts principally by diminishing the force of cohesion is, that a metal which cannot be oxidized but at an elevated temperature, is oxidized at that of the atmosphere if it is dissolved by mercury: and thus phosphorus, dissolved in hydrogen, inflames at a much lower degree of temperature than when it is in a solid state.

When an elastic substance is reduced to a liquid state by combination, it acts like the liquids, while the action it experiences, does not change; but as soon as that begins to diminish or the temperature is raised, the elasticity it acquires is to be considered as a force, which, added to the preceding, influences the results, as is done by the force of cohesion in an opposite sense.

157. The gases exercise also a mutual action on each other, and they exercise one on liquids and on solids; so that if these have the property of

causing them to lose their elastic state, they can, reciprocally, reduce these to their own state; but this action varies greatly in its results, according to the intensity of its action, and according to the circumstances which accompany it. Besides the liquids can take the gaseous state by an elevation of temperature, which is different for each of them, and then their chemical action is changed. All these subjects required a strict investigation.

Cavendish observed* that on agitating a mixture of ten parts of atmospheric air and one part of carbonic acid, with an equal volume of distilled water, this only deprived the air of half the carbonic acid; having transferred the air over fresh distilled water, it absorbed only half of the remainder of the carbonic acid, as was shown by a subsequent absorption by lime-water.

I have ascertained† that if, in the combustion of a carburated, or oxicarburated hydrogen gas, there is a residue, it retained near a tenth of the carbonic acid formed, notwithstanding it had been agitated over a considerable quantity of water: it is by this action which the air exercises on carbonic acid that it can deprive water of that which it holds in solution; hence it arises, that when an acidulated water is enclosed in a vessel with a certain quantity of air, this makes an effort to escape, and overcomes the obstacles opposed to

* Exper. on Air. Philos. Trans. 1784.

† Mém. de l'Instit. tom. iv.

the dilatation it experiences by the accession of the carbonic acid if they are too weak ; but the action of the air is limited by the quantity which can exercise it, and by the action of the water, which increases as the quantity of the carbonic acid is diminished.

We discover, therefore, in this action of the air on the carbonic acid, all the circumstances which accompany that of chemical affinity, with the difference produced by the elasticity, which augments the action of the air on the carbonic acid, relatively, when it increases the energy, either by an elevation of temperature, or by a diminution of compression.

This property of the gases may be considered as general, since it has been observed in those whose specific gravity, which is opposed to its effect, has the greatest difference.

Vassali who has made some interesting observations on this subject* recollects that ten years before, Volta had shown him that hidrogen gas descended through atmospheric gas for the purpose of spreading itself equally through the whole mass, and that it required some time to attain an equal diffusion : he consequently made experiments himself which confirmed this property, and he also ascertained that, possessed by carbonic acid, of being equally dissolved in a mass of air, in a sufficient space of time.

Mém. de la Soc. Méd d'Emul, 3^e Année.

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We must therefore admit a reciprocal action between the gases, comparable to that which produces the solutions of liquids in each other, or of solids by liquids; but it has its peculiar characters.

158. When different gases are mixed, whose action is confined to this solution, no change is observed in the temperature, or in the volume resulting from the mixture; hence it may be concluded, that this mutual action of two gases does not produce any condensation, and that it cannot surmount the effort of the elasticity or the affinity for caloric, so that the properties of each gas are not sensibly changed, while in the mutual solutions of liquids a condensation takes place, and in that of solids there is frequently observed a dilatation accompanied by a production of cold which is owing to the reciprocal affinity opposed to the combination with caloric being diminished; thus, although both the solution and combination of two gases are the effect of a chemical action which only differs in its intensity, a real difference may be established between them, because there is a very material difference between the results: the combination of two gases always leads to a condensation of their volume and gives rise to new properties; in their solution the gases share in common the changes arising from compression and temperature, and preserve their individual properties, which are only diminished in the ratio of the slight action which holds them united.

When

When liquids dissolve a gas, this loses considerably of its volume and condenses, for water which dissolves an equal volume of carbonic acid changes its specific gravity very little; this solution has, therefore, the characters of combination; but when by its action the air disengages this acid from the water, it regains the volume which corresponds to the temperature and to the pressure, and receives, for that reason, the caloric which its dimensions require.

In this instance, therefore, we find a result of the reciprocal action of two substances which is very different, because of the respective state of condensation in which they are; as the liquids are capable of taking the properties of the gases by the action of heat, and can dissolve in the air and in other gases, we must examine the relations which exist between their different states and the forces which are put in action to produce them.

159. In the first place let us apply to water, reduced into the vaporous state, the observations which have been made, (108), on the action exercised by caloric on the gases.

If the temperature is above that of ebullition, and if the pressure remains the same, the vapour of water agrees in every respect with the other gases, as has been proved by the experiments of Gay Lussac (108), and there is not any thing to be observed which concerns it in particular: when it is only at the boiling point, at a temperature of 100° of the centigrade thermometer, and under

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under a pressure of 28 inches, it has a degree of elasticity which corresponds to that temperature, and by which it retains its gaseous state; if the pressure is then diminished, it continues to dilate like another gas, and its tension diminishes in the ratio of its dilatation, or of the power of its spring compared with the space. (*Note V.*) In this state it can receive an addition of vapour proportionate to the augmentation of the volume until it has acquired the degree of tension which it had at first; but if the space is reduced to its first dimensions, all that part of the vapour which was added, is restored to the liquid state, and the quantity of that which remains, as well as the elastic tension, is the same as that which existed at first.

If the temperature is lowered, it can no longer preserve the elastic state, it yields in the same manner to the pressure which has been supposed, and is reduced into a liquid, which nevertheless preserves an elastic tension corresponding to the actual degree of temperature.

If the pressure alone is augmented, it still resumes the liquid state, and the water re-produced exercises an elastic effort which answers to the tension of the vapour which would have been formed under another pressure.

160. Let us now compare the vapours with the state of the liquids which are held in solution by the permanent gases.

Water which is dissolved in the air acquires the elastic

elastic state: Deluc observed * that humid air was lighter than dry air; but he considered the elastic vapour of the water as simply mixed with the air, and as having a tendency to separate itself from it, and to rise by the difference of its specific gravity.

Saussure proved † that the air acted like a solvent; he modified the theory of Leroi, who was the first that had this idea, but who compared this solution to that of a saline substance; he showed that water is reduced into the state of an elastic fluid by being dissolved in the air; that the volume of this is affected by it, according to the pressure and the temperature, until the point of saturation at which the dissolution ceases to operate, so that in the state of complete saturation, a cubic foot of air only holds about eleven grains in solution, at a temperature of 15°; and that this quantity diminishes by a reduction of the temperature; but with respect to the effect of pressure on the elastic vapour, his opinion offers some uncertainties which I shall discuss; I shall then deduce, from the observations of this celebrated philosopher, the consequences which appear to me to result from them, and, finally, I shall endeavour to establish these consequences by other observations.

Having withdrawn, by means of an air-pump,

* Recherch. sur les Mod. de l'Atm. § 709.

† Essais sur l'Hygrométrie,

the eighth of the volume contained in a receiver, Saussure observed that the hygrometer moved towards dry; by repeating similar operations, the progress of desiccation was continued, nevertheless the hygrometer did not move in a uniform manner, it indicated an excess of humidity, which was greater as the quantity of air diminished, and when the pump could not produce any further effect, the hygrometer remained fixed at 25° from extreme drought.

161. We must in this case distinguish the indications of the hygrometer from the real humidity; when Saussure had completed his experiment without being able to bring the hygrometer further than 25° from drought, it would doubtless have been possible to have caused it to pass to the degree of extreme drought by the action of the alkali which Saussure employed for that purpose, since all the airs, however they may have been dilated, are brought, by this means, to the point of the greatest drought; but if water had then been introduced into the receiver, the hygrometer would have begun to return to the 25° at which it had stopped, and would afterwards have moved as far as extreme humidity: the quantity of water necessary to produce extreme humidity, in a given temperature, is therefore equal, whether the space be void, or whether it be filled by an air more or less dense: this does not invalidate the difference of the indications of the hygrometer, in an air more or less dense, deduced from direct observa-

observations ; the conclusion to be drawn from it is, that, in a vacuum, the hygrometer may retain a little humidity which is not naturally reduced to vapour.

Other observations of Saussure seem to me to prove, that when the hygrometer approaches extreme humidity, or the term of its action, it follows a contrary movement, and that it acquires the equilibrium of humidity with difficulty, so that the quantities of water are greater than its motion indicates ; "thus," he says, § 333, "when the hygrometer is at 70° , there must be, according to my table, a production of cold of $12\frac{1}{2}^{\circ}$ to bring the air again to the term of saturation, and nevertheless I found one day, when the hygrometer was at 70° and the thermometer at 10° , that the exterior surface of a glass began to be covered with dew, when the water contained in this glass was only $8\frac{1}{2}^{\circ}$ colder than the air."

Saussure gives himself the explanation of the disagreement of the hygrometer with the real humidity of air a little condensed : he says, § 146, "according to the general laws, the air must attract the particles of vapours with less force when it is rare, when its moleculæ are few, than when it is dense. Consequently the hair, from which the rarefaction of the air takes none of its attractive force, must have a greater relative force of attraction in a rare air than in a dense air; and by this alone it must absorb a greater quantity

“ quantity of vapours, and indicate a greater humidity than it would do, in similar circumstances, in a dense air. Thus, although the air on quitting the receiver may have carried with it a moiety of the vapours, that moiety which is left, being more strongly attracted by the hair than by the rarefied air which remains, affects this hair more than it would have done, if the air had retained all its density; and thus the hygrometer indicates a greater quantity of vapour than really remains in the receiver.”

I cannot, therefore, adopt the consequence which he draws from the same experiments, and which he establishes as a principle in the sequel of his work, § 148: “that in proportion as the air becomes more rare, it requires a smaller quantity of water to saturate it. For example, if at the summit of Saint-Bernard 8 grains $\frac{6}{13}$ produce the effect which $9\frac{1}{2}$ would have produced in the plain, it would only require, under similar conditions, $\frac{8\frac{1}{2}}{13}$ of the quantity to saturate the air of Saint-Bernard, which would have been necessary in the plain: and by applying the same reasoning to the same experiments, it will be seen, that if the air was rarefied so much as only to sustain $2\frac{1}{2}$ lines of mercury, it would only require, for saturation, the twentieth part of that which it requires when the barometer stands at 27 inches.”

162. It appears to me, therefore, that even the experiments of Saussure show directly, that the ponderable

ponderable quantity of aqueous vapour is the same, in the same space, whatever the quantity of air may be with which it is united; that the temperature alone determines this quantity; that it maintains its tension independently of the differences of pressure, as though it was a permanent gas, so that it contributes to the elastic effort whatsoever may be the volume to which it may be reduced by the compression of the air, in the same manner as a correspondent quantity of air at different pressures.

The experiments of Saussure have also proved, that the tension of the elastic vapour of water is proportionate to the quantity dissolved in a volume of air at a given temperature: as these experiments are fundamental, I shall relate the process by which they were performed.

A barometer enclosed in a well luted globe is only sensible to the elasticity of the air; on this account Saussure called it a *manometer*.

He placed therefore in a large globe a manometer, a thermometer and two hygrometers to compare the effects of the elasticity, the humidity and the heat: he introduced successively a small roll of linen moistened and weighed very exactly; he withdrew it when it had produced a determinate effect on the manometer; thus he was enabled to compare the effect of a weight of water on the elasticity of the air contained in the globe. He pursued a contrary course by plunging a jar containing desiccated pot-ash into a globe filled with

with humid air, and by comparing the augmentation of weight which it acquired with the diminution of pressure observed in the manometer he obtained results corresponding with the preceding.

He concluded from his experiments, which were made with great care, and after making the corrections in the result, required by the variations of temperature which had supervened, that the specific gravity of the elastic vapour of water is to that of the air, at the same temperature and under the same pressure, as 10 to 14.

163. Deluc (*Note XII.*) and Volta have also made numerous experiments, which prove that the quantities of elastic vapours which are formed in a vacuum, are exactly the same as those which occupy the same space filled with air, at the same degree of saturation whatsoever may be the compression: it is to be hoped that the latter will not delay the publication of the experiments he has made on this subject, and which he has been so kind as to communicate to me. But these two philosophers concluded that the water was not held in solution by the air, and that it was indebted to the action of caloric alone for its state of elasticity, independently of all affinity for the air.

If this opinion was well founded, it must be supposed that a liquid, which tends to assume the elastic state, would only penetrate the air on account of the vacancies it could occupy, and that its

its elasticity would correspond exactly with the quantity of these vacancies ; and, from this, it would follow that the volume of the air could not increase, but it does increase precisely in the ratio of the elastic fluid which is formed. Can it be said with Deluc* that an attraction, similar to that which causes the ascent of liquors in capillary tubes, distends the pores of bodies which are moistened ? And has not an attraction which unites one substance to another, and, which overcomes the resistance of its moleculæ, all the characters of chemical affinity ? This opinion cannot be reconciled with the facts which prove that the gases mutually dissolve each other so as to form a uniform gas notwithstanding the difference of specific gravity, as has been shown by Volta himself ; and the same thing takes place with liquids which dissolve in the air ; nor is it more compatible with the uniform compression exercised by the atmosphere on liquids.

164. This compression and the mutual solution of the gases prove, that while vapour exists in a space, there is not a vacuum in the sense usually attached to the word ; for an uninterrupted action exists between all the moleculæ which are therein, which is only weakened in proportion to their distance from the moleculæ which form the centre ; and if radiant heat and light pass through the gases, it is because the motion peculiar to them

* Philos. Trans. 1791.

is superior to the action they meet with, and is not sensibly weakened by it.

It therefore appears to me incontrovertible, that it is a true chemical action which produces the solution of liquids in the gases, and evaporation, as has been advanced by Saussure. But observation confirms the opinion of Deluc and Volta, respecting the quantity of elastic vapour formed in a given space, and which is equal, whether the space is empty, or occupied by an air more or less dense, but which is at the same hygrometric degree, and at the same temperature.

165. The experiments of Saussure have proved directly that the tension of the elastic vapour of water is proportionate to the quantity which dissolves in a volume of air at a given temperature, and that it then acts as a gas whose specific gravity is to that of water, as 10 to 14: whence it follows, that a judgment may be formed of the effect of a liquid which is reduced to the state of an elastic fluid by the tensions found at a given temperature, even in a vacuum, as will be confirmed by the following observations; but to ascertain its relation with the quantity of the air, when it is dissolved by it, the specific gravity of the elastic vapour which it forms, must also be known as that of the elastic vapour of water is known.

The difference produced by the pressure of the air in this vapour, does not alter the relation of its specific gravity, so that that which would have

have filled a void space with a pressure of six lines, will only fill the 54th part, if the air saturated with this water can raise the column of mercury to 27 inches, while, when dry, it could only raise it $26\frac{1}{2}$ inches.

Van Marum, on carefully repeating the experiments of Lavoisier and Laplace, observed* that when water, ammonia, and ether, were introduced into different barometer tubes, placed on a bath of mercury, the temperature being 10°. the water caused the mercury to descend 0.4 inches ; the ammonia, 7.2 ; and the ether 12.5.

Saussure found that the air being saturated with water at 16°. of Reaumur's thermometer, and consequently at a higher temperature, and at a pressure of 27 inches of mercury, the water contributed to the elastic effort, by nearly six lines of mercury : these two numbers coincide as much as could have been expected, and correspond with the experiments made by Deluc.

166. When the air is saturated with ether at different temperatures, it acquires also the same tension as in a vacuum at corresponding temperatures, as Volta ascertained by very delicate experiments.

Consequently, ether having, at a temperature of 10°. a tension of 12.5. it is reduced by a pressure of 15.5. to the state it was in when dissolved to saturation by the air at 28 inches of pres-

* Descr. de quelques appareils chimiques.

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sure; the air also experiences a compression in the manometer: in the following section we shall see the effects which result when the two gases acquire the liberty of dilating.

The difference which there is between the vapour of ether which is alone, or which is dissolved in air, is, that when there is a vacuum, if the tube is lowered in the mercurial bath to a quantity equal to the dilatation, as was done by Van Marum, all the elastic fluid is restored to liquidity; but if the solution of ether in air is compressed, the volume of this diminishes in the ratio of the compression, and the ether only regains the liquid state, in the ratio of the diminution of the space.

167. This last experiment is well calculated to show the effects which I analyse: let a solution of ether in air be compressed over a mercurial bath, it will be seen that the ether will be reduced into drops or even into a stratum of liquid, as the compression increases: the drops will disappear and the transparency of the tube will be restored by afterwards causing a dilatation of volume equal to the first.

All the effect of the compression is then confined to causing a part of the elastic fluid to take the liquid state, and the tension of that which is in solution remains the same; we must therefore distinguish the effect of the reciprocal compression, in which the elastic vapour seems to resemble the other gases, from that compression which produces

produces a diminution of volume. We have seen (*Note V.*) that the tension of the permanent gases only appeared to be augmented by compression, because by it, the number of the springs applied to one surface, were multiplied; this effect does not take place in elastic vapour, because it can, with more ease, resume the liquid state.

168. It may therefore be established as a principle, 1st. That air dissolves the evaporable liquids by the action of its affinity; 2d. That in this solution they take the form of elastic fluid, and, in that state, have all the properties of elastic fluids as far as the term of saturation.

It follows from this that the water held in solution by the air, acquires from the elastic state thus procured to it, exactly the same properties as it has when reduced into vapour by the sole action of heat; so that the action of the affinity of the air consists in maintaining the water in an elastic state, and in communicating to it the properties of a permanent gas, as far as the term of saturation: what is said of air and water, may be applied to the other solutions of liquids by the gases.

The property by which the air maintains the vapour of water in the elastic state to the term of saturation, may be compared to that, which, according to an observation of Blagden, which I have already mentioned, belongs to the muriate of soda, of maintaining water liquid to a certain degree below the ordinary point of congelation; so that it then suffers, by the cold, a progressive de-

crease, as simple water does at a higher degree ; but when, at length, it arrives at the term of its congelation, it experiences a dilatation similar to that observed in simple water which approaches congelation, and resumes the properties which belong to it.

169. Hence it follows that the elastic vapour of water experiences, by the elevation of the temperature, the same dilatation as the other gases, and consequently it has the density of the vapour of boiling water, when it reaches 100° of the centigrade thermometer.

Saussure has proved (161), by comparing the quantities of water which he dissolved in dry air with the increase of tension which resulted, that there was a constant relation between the tension and the vapour produced ; and that this elastic vapour has a specific gravity which is to that of water as 10 to 14 at equal temperature and pressure. Now Lavoisier concluded from his own experiments that the specific gravity of the air, at 10° of the thermometer, was to that of water as 842 to 1 ; which gives a specific gravity of 1570, estimating the augmentation of the volume of the vapour of water at $\frac{1}{3}$ from 10° to 80° of the thermomètre.

We are indebted to Watt for the most correct information relative to the specific gravity of the vapour of water at the boiling point : he expresses himself thus ;* *it is known from some of my ex-*

* Philos. Trans. 1784, p. 352.

periments

periments and from those of Doctor Black, that the vapour of water, reckoning from 60, or temperate, is more than twice the volume of an equal weight of oxigen gas.

Although this indication is a little vague, and although we cannot reckon on perfect accuracy in Saussure's results, the most satisfactory correspondence will, nevertheless, be found between the first result and that of Watt: for, according to the determinations of Lavoisier, the specific gravity of oxigen gas, at 10° of Reaumur, is 765; so that the declaration of Watt fixes the specific lightness of the vapour of water at more than 1530.

170. By ascertaining that the air acts on the liquids which it dissolves in the same manner as on the other gases, it is also proved that the elastic vapours must be found in the same quantity in a vacuum, or in a space filled with air, while the temperature and the tension or saturation remain the same: for to produce a different effect it is requisite the air should act differently on a gas by compression than it does; and that it should exercise a different force on the vapour of water than on another gas, and then there would be a difference between the effects.

When, therefore, compression diminishes the space which contains a saturated air, a part of the elastic vapour must become liquid to permit the other to occupy the space suitable to it, as would have been the case if the space occupied by it had been

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been diminished by the effect of its elastic force alone, or as would have taken place with the vapour of water at the boiling point. There is this difference between liquids, that, at the same temperature, their tensions, which correspond with their elasticity, are unequal until they reach ebullition; then their tension is equal to the resistance of the pressure of the atmosphere; they are changed into elastic fluids, and follow the same laws of dilatation: before this degree of temperature the affinity of the gases gives them the properties of permanent gases, but without producing any change in the term of their greatest tension; neither does the reciprocal action of the permanent gases influence the tensions they have in those circumstances.

171. Saussure thinks that the air does not dissolve the water but *when the action of fire has converted it into elastic vapour*, § 191. In this I differ from his opinion: the action of the air and that of caloric are simultaneous; but it is the first which determines the second, the pressure of the atmosphere opposes the formation of the vapour by all the excess which it has over the tension of the liquid; thus in the circumstance in which Van Marum's experiment, which I have quoted, was made, a pressure of 15 inches of mercury was sufficient to prevent the production of the vapour of ether, and could also restore it to the liquid state when it was formed.

The action of the affinity of the air on water is manifested

manifested in a striking manner in the solution of ice, notwithstanding the resistance of the force of cohesion. Saussure observed that at 2.7° below the freezing point, the hygrometer which was at 36.70° rose, in the air in which he had put a frozen cloth 18° in one hour, and in three hours 49.52° . Nevertheless it only reached 86.22° in that space of time, so that the obstacle of the force of cohesion not only retards the dissolution, but probably prevents its completion. It is very likely that the effect was diminished by the reduction of the temperature, and that, at last, it attained a degree at which the dissolution could proceed no farther.

172. Since the elastic vapours which the liquids can produce are determined by the space, and since the pressure they experience when in a state of solution cannot vary their ponderable quantity, it may be conceived how Saussure found the same hygrometric properties in hidrogen gas, atmospheric air, and carbonic acid. Priestley had observed before that the different gases took the same increase of volume when they were brought into contact with ether : I repeated these experiments with Gay Lussac on oxygen gas, azote gas, hidrogen, atmospheric air, and carbonic acid, and we observed that they all experienced the same dilation, except the carbonic acid gas, in which it was a little slighter ; but this difference, which was very small, may be naturally ascribed to a little carbonic acid which might have been reduced to the

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the liquid state by a portion of the ether. We see that water dissolves equally in a similar quantity of the different gases, and that it retains a tension proportionate to the temperature and to the state of saturation.

173. Nevertheless, it must not be concluded from what precedes, that gazeous substances do not hold other water besides that which is in the gazeous state, and on whose volume they do not act by compression, but as they act with each other; I shall prove, on the contrary, that some of them can hold it in true combination: but it is not that which produces the hygrometric effects, because being retained by a stronger affinity, it neither contributes to the humidity nor to the dryness of bodies which partake of the air of the atmosphere: thus, clay retains a certain quantity of water which it does not abandon but at extreme degrees of heat, and which hygrometric substances are very far from being able to take from it.

The reciprocal affinity of the moleculæ of water, which terminates by reducing it to a solid body, when the force opposed to it becomes too weak, also produces effects between the vapour of water and the liquid: hence it arises, as has been observed by Gay Lussac, that when a substance, which yields aqueous vapours but no permanent gas, is distilled, without communication with the air, and these vapours are received into a vessel filled with water, a partial vacuum cannot be avoided.

avoided which causes the water to return into the retort; but this inconvenience may be easily prevented by interposing a small stratum of mercury between the water and the retort.

Welter had previously devised a method of employing the pressure of the atmosphere itself to prevent this effect by tubes of safety, which since that time have been used with success in a great number of operations, and which have given so much utility to Woulfe's apparatus; but when it is essential to avoid the mixture of the air, the first method is greatly superior, because the mercury having much less affinity with the vapour of the water than the water itself, the effects of the absorption, which are very difficult to avoid, do not take place.

It is by an analogous effect that, in steam-engines, a small quantity of cold water produces a sudden condensation, the effect of which is seconded by the dilatation which takes place in the remainder of the vapour, and by the cold which accompanies it, as was observed by Darwin.* This reciprocal action also explains the effect of the water which favours the disengagement of a gazeous substance; whence it arises, that the absence of water, as has been shown by Withering,† distinguishes the native carbonate of barites, which cannot be decomposed by heat, from the

* Philos. Trans. 1788.

† Ibid. 1784.

artificial carbonate, which can, on account of the water it contains; but the first may be decomposed in a tube by passing a current of steam through it, as was done by Priestley, or by supplying its place with a current of air, according to Clement and Desorme.

174. When, therefore, the water is feebly retained in a combination, and is reduced into vapours, it solicits and disposes another substance to take the gaseous state by all the affinity it has for the gas which it dissolves. This property may be of great utility in many of the operations of chemistry,

The mutual affinity of the gases can, therefore, produce between them an effect which is greater than their difference of specific gravity, but which is inferior to the elastic tension which belongs to each molecule of both, so that the volume is not changed by this action: the liquids which take the elastic state comport themselves afterwards like the gases.

Some solids seem to dissolve in the air like liquids: thus, phosphorus dissolves in azote and increases its volume, and the interesting observation of Gay Lussac on muriate of ammonia (108) proves that it does the same: it is probable that odoriferous substances also dissolve, since, in their union with the air, they retain their characteristic properties; but if the mutual affinity of the gases is stronger than that which is confined to solution, and if it can effectuate a change in their respective

spective dimensions, it produces other phenomena which belong to combination, and which is widely different from what I designate here by solution, because for the same reason that the respective dimensions are diminished, the reciprocal action is increased, and the effect is only limited on account of the saturation produced.

175. Solution must be distinguished from combination, not only because in the first, each of the substances is retained by an affinity so weak that it preserves its dimensions; but also because all the properties which characterise it, all its other tendencies to combination are scarcely weakened; whereas in combination the opposite properties are diminished by all the saturation they have experienced.

There is, therefore, in the combinations of the gases a condensation which is usually greater than that observed in liquids, because they are susceptible of a much greater diminution of volume from the same causes.

In fact, a condensation, which is sometimes considerable, is observed in the gaseous combinations which are formed; thus, the vapour of water at the heat of ebullition occupies much less space than the hidrogen gas and oxigen gas, which produce it, would have occupied at the same temperature: nitrous gas has a specific gravity greater than that of the simple mixture of its two elements; it is the same with ammoniacal gas.

The

The approximation of the moleculæ may be such, that the reciprocal action shall be augmented to a point at which the combined substance takes the liquid state, or even the solid state; thus ammoniacal gas, in which the elements are already greatly condensed, experiences a new condensation when it combines with muriatic acid gas, and both take the solid state.

Hidrogen gas and oxygen gas reduced to water, can only preserve the gaseous state under a certain degree of pressure; at a pressure too great, they take the liquid state, and finally by a diminution of temperature they become solid. This combination is therefore, from the approximation of the moleculæ, in an intermediate state between that in which the reciprocal affinity does not produce any sensible effect, and that in which it produces liquidity and finally solidity, according as the state of the temperature and of the pressure, the expansive force, or the force of cohesion, becomes preponderant.

176. There is found, therefore, in the gases which combine, and which undergo a sufficient condensation, the same phenomena as I have spoken of in the other combinations in which the disposition to solidity is augmented whenever the affinity has sufficient energy; but they are much more obvious in these because the condensation is much greater.

The liquids and solids which combine with gaseous substances reduce them to their state, or take

take the gaseous state themselves, according to the energy of the forces which are in action, or sometimes according to the proportions.

When a solid enters into combination with an elastic fluid, it is difficult to estimate the condensation which results from the combination, because it is not known what volume the solid would take at a low temperature, if the force of cohesion ceased to act; nevertheless, the condensation is manifest, since, in most cases, the volume of the gaseous substance is reduced by combination, and, in all cases, the specific gravity of the combination is greater than that which the gaseous substance had; thus the specific gravity of oxygenated muriatic gas, of sulphureous acid, and of carbonic acid, is much greater than that of oxygen gas: that of carburated, sulphurated, or phosphorated hydrogen gas, is much greater than that of hydrogen gas.

177. If, in the combinations which are formed, a portion of caloric is always eliminated; if the immediate effect of the action of caloric is, in all cases, the dilatation of bodies; and if it augments their disposition to elasticity, it appears at first difficult to conceive how an augmentation of caloric can produce the combination of hidrogen and oxigen from which a great quantity should be eliminated; and how it happens, according to the observation of Monge,* that, by augmenting the

* Mém. de L'Acad. 1783.

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dose of the solvent, the adherence which it had to its bases is diminished.

I have borrowed from Monge himself an explanation which seems to me to resolve this difficulty.* Compression by causing the moleculæ of two gases to approximate augments their reciprocal action; it may be carried to a point at which it causes combination: now that part of a gas which first receives the heat experiences a dilatation which is greater in proportion as the heat is more intense, it compresses, with a strong effort, those parts of the gas which have not yet received the same degree of temperature, by that means it determines them to combine; but the caloric which abandons this combination, and which raises it to a much higher temperature, produces, by the tension which is the consequence, a much stronger re-action, so that the part which at first only dilated, is itself compelled to enter into the combination.

The caloric therefore only causes, by the dilatation of one part of the gas, a compression on that which is less heated, but the total of the effect is owing to the sudden approximation of the moleculæ produced by the combination, as it is produced from the same cause in the percussion of solid bodies, and in that of bodies which contain substances whose combination requires only a slight cause, and which may be said to be at the limits of their existence.

* Mém. de l'Acad. 1788.

Trembley has made some observations in opposition to this explanation which seem to me to arise only from the want of clearness with which I have offered it. He says,* " how then can caloric produce elasticity and compression at the same time? and a compression by which it drives off the aggregates which it had formed with the oxygen? In the first case, a new and unknown agency is admitted, which was foreign in the theory, and proves its insufficiency: in the second, effects so different and so opposite are ascribed to the caloric, that it is impossible to form any idea of them, and by that means we fall into the same error with which the phlogistic system has been so much reproached."

Trembley has therefore founded his objection on the supposition that the caloric augments the elasticity, at the same time that it produces a compression which drives off the combination it forms: this is not my meaning.

The sudden dilatation, produced in one part of the two gases, which are mixed, or in simple solution, causes, according to the explanation which I think should be adopted, a proportionate compression in that part which has not yet been able to partake of the temperature, and thus produces the combination of the two elements.

1st. Compression favours the combination of a

* Mém. de Berlin, 1797.

some element, naturally elastic, in their composition, receives therefore from the changes of its constitution, modifications, whose conditions must be determined, as well as their characteristic differences, from those of the substances which do not, sensibly, change their constitution; I shall therefore in this chapter compare the differences which distinguish the decomposition of these substances.

I call that *resulting affinity* whose action proceeds from several affinities in the same substance, while this exercises it collectively, and I distinguish that of the parts which compose it, when they become individual, by the name of *elementary affinities*: for example, when nitric acid, which is composed of oxygen and azote, combines with pot-ash, it acts on this alkali by an affinity which results from that of the oxygen and that of the azote; but if the elementary parts separate to enter into other combinations, the elementary affinities are substituted to the resulting affinity. As chemical action is reciprocal, I give, in like manner, the name of resulting affinity to that of a simple substance for a compound substance, whose composition it does not change.

179. If water dissolves a saline substance without changing the respective state of saturation, and if it is incapable of causing any change in it, whatsoever may be the proportion in which it is made to act, it may be truly said that the reciprocal action of the saline substance is resulting:
which

which proceeds from the elementary parts of the combination being again removed from a state of saturation, so that what they retain of their reciprocal tendency, unsatisfied, is more considerable than the action which the water exercises on one of the elementary parts, in preference to another; but if the water acts on oxygenated sulphate of mercury, it produces a separation of the elementary parts, it changes the state of the combination according to the quantity and according to the temperature which assists it, then all the forces which influence the result must be compared, as individuals: the water must no longer be considered as a simple solvent.

The species of resulting affinity I have just mentioned, and which belongs to the solvents properly so called, does not require any particular consideration here; it is sufficient to remark that, if a solvent acts without changing the state of the combination, or, if an action comparatively stronger does not permit the same relations to remain between the elements of the combination, in the first case, the liquid does not sensibly change the state of the forces, it simply acquires the faculty of exercising them by giving liquidity; in the second, by changing the state of the combination, it leads to another result, by the force which it exercises, but without sensibly changing the forces which acted before its intervention: it is not the same when the elementary substances change their state by entering into other combina-

tions; then the forces which act experience a revolution which it is proper to distinguish, and of which we must consider the cause and the effects.

180. The action of a substance depends on the energy of its affinity and of the quantity with which it meets, in the sphere of activity; if, therefore, the elasticity it is supposed to have in the free state is overcome by the action of another substance; if by that it is much condensed; and, if the combination it forms is liquid, it enjoys all the properties of liquids and can act with a much larger mass.

Nevertheless the effect of its affinity is diminished by all the saturation it experiences from the combination it enters into; but this effect is frequently much less in the resulting affinity, than the augmentation of energy which it acquires by its condensation. Besides, if the substance with which it is combined has become liquid, although its action may be, in like manner, weakened by all that which it exercises on the gaseous element, it nevertheless acquires more advantage from the liquidity than it loses by the combination, and concurs with the action of the gaseous substance.

By this it is seen how sulphur and phosphorus, by condensing oxygen can form combinations which have so powerful an action on alkalis, and whose properties are principally derived from that of the oxygen, while, in the gaseous state its elasticity

ticity was an obstacle to all combination with them.

181. From what has been said it must not be concluded that the greater the condensation of a gazeous substance is, the more considerable is the energy it exercises in all its effects; but there are two conditions which must be distinguished, the condensation and the diminution of the affinity by the saturation it experiences.

The stronger the condensation is, the greater is the loss arising from the saturation, other things being equal; in a combination, there will therefore be found less of the properties which are owing to the affinity of a gazeous substance, in proportion as the substance is reduced to a greater state of condensation.

The sulphureous acid contains a smaller proportion of oxygen than the sulphuric acid, but it is less condensed, and, for that reason, more volatile; it even quits the gazeous state with difficulty, which has caused it to be considered as weaker; nevertheless it possesses the acid properties in a greater degree, for if the sulphite of pot-ash is exposed to oxygen gas, it absorbs a considerable quantity, and all the sulphite is converted into sulphate, without there being any change in the state of saturation, and without any disengagement taking place, as I have satisfied myself by making the experiment in a receiver filled with oxygen gas over water.

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I shall notice in this place that in the estimations which have been given of the proportions of acid and alkali in the sulphites and sulphates, there is necessarily an error in fixing the proportions of sulphureous acid in the sulphites as greater than those of sulphuric acid in the sulphates.

When a sulphite is urged by the fire, sulphur sublimes, sulphureous gas is disengaged, and the residue is found to be converted into a sulphate, which induced me to believe that less sulphur was retained in the sulphuric acid which remains combined with the pot-ash*; but a part of the alkali is in excess, and is in the state of sulphuret, so that the conclusion I had drawn from this experiment is not correct.

Nitrate of pot-ash from which a portion of oxygen has been disengaged, dissolves afterwards with facility in water; the solution does not yield any trace of alkalinity, as has been ascertained by Gay Lussac; nevertheless much nitrous gas is disengaged when an acid is poured upon it; but the action of the fire must not be urged too far, because then the nitrous acid itself will begin to be decomposed, and the alkalinity will be developed: nitrous acid therefore has as much acidity as nitric acid.

The oxygenated muriate of pot-ash, by the action of heat, abandons all its oxygen gas, and

* Mém. de l'Acad. 1782.

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nevertheless the residue is still perfectly neuter, although the contrary has been advanced.

There can be no doubt that the phosphites might be converted into phosphates, as the sulphites are into sulphates, without the state of the saturation being changed.

182. These facts prove that the acid property which consists in saturating determinate quantities of an alkali, is not proportionate to the quantity of oxygen which combines with a base; but that the more it is condensed, and, consequently, the stronger the action which it experiences, the less acidity does it give to an equal quantity, because the acid property communicated by the affinity which remains free, is diminished in proportion to that action.

But the properties it owes to the condensation are much greater in sulphuric acid; it requires a specific gravity much more considerable, and consequently has much more power against the force of cohesion (49), and is much more difficult to decompose.

This correspondence of action can only be established between acidity and the condensation of oxygen, when the base is the same, and not when the comparison is made in its different combinations, because the properties of the base also contribute to the action it exercises on the alkalis, and may modify its effects in a certain degree: sulphur and phosphorus offer an instance: they have nearly the same specific gravity; phosphorus acts much

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more powerfully on oxigen than sulphur does, so as to fix it in a larger quantity and in a greater state of condensation, and by that means, phosphoric acid acquires greater specific gravity and much more fixity than sulphuric acid: nevertheless, if the experiments which have been made to determine the proportions are exact, it will be seen that the oxigen produces a more powerful acid effect in phosphoric acid than in sulphuric: 100 parts of sulphuric acid, according to the experiments of Chenevix, which differ but little from those of Thenard,* contain 38 ponderable parts of oxigen, and according to Lavoisier 100 parts of phosphoric acid contain 60 of oxigen. Now, 100 parts of sulphuric acid, or 38 parts of oxigen neutralize 70 parts of lime†; while 100 parts of phosphoric acid, or 60 parts of oxigen, neutralize 174‡; nevertheless it seems to me probable that there is a circumstance which leads to error: I have observed that the phosphate of lime, in precipitating, takes an excess of lime, so that it is possible that the phosphate obtained by Vauquelin, had a portion of lime which exceeded the neutral state, and, if the experiment was made with a phosphate exactly neuter, it might be found that oxigen communicates a smaller proportion of its acid properties in its combination with phosphorus, than in that with sulphur.

* Bibl. Britan. tom. XVIII.

† Syst. des Conn. Chim. tom. III.

‡ Ibid.

183. By applying the principles which these observations seem to establish, to the different combinations formed by the elastic substances, a judgment may be formed from the properties of these combinations, of the state of saturation they experience: thus as water does not permit any property of oxygen or of hidrogen to be perceived, it may be concluded that these two substances are combined at the point at which the reciprocal affinity exercises the greatest effect, and that they are in a state which may be compared with that of a neutral salt in which the acid and alkaline properties have equally become latent: they have experienced by their combination a condensation by which their volume has been reduced to $\frac{1}{200}$. In acids, the qualities of the oxygen remain predominant; in inflammable liquids, it is those of hidrogen which are so; so that in combinations of the first description, the oxygen experiences a less degree of saturation than in water, and in those of the latter, the hidrogen is in that situation.

These observations convince us that in the gaseous combinations, there are properties analogous to those we have observed in the combinations of acids with alkalis; saturation renders the characteristic properties of the two gases latent; but those which belong to one of the two may not be neutralized, as is the case in acidulous and alkaline salts; then the combination retains the distinctive properties of one of the elements; this is

is what takes place in the acids which owe their acidity to the oxygen. Its influence is the greater in proportion as it experiences less saturation, it is from this cause that it retains as much capacity for saturation in sulphureous acid than in sulphuric acid, although it is in a smaller proportion; nevertheless it must, for this purpose, have acquired enough of solubility in water to be able to act with a degree of concentration sufficiently considerable; because, if it cannot be enough condensed, it will, by its state of dilatation, lose that which it could have gained from the weakness of the combination, as is observed in oxygenated muriatic acid. Finally, in gazeous combinations, as in those of acids and alkalis, the effects depending on the condensation must be distinguished from those which proceed from the saturation.

184. After these general considerations of the combinations of gazeous substances, we shall examine the resulting action of these combinations, and the modifications it experiences.

While a substance acts by a resulting force, the relative state of its elementary parts does not change; as for example, we must not consider a mixture of nitric acid and sulphuric acid in water as a solution of oxygen, azote and sulphur, nor should it be done with respect to those substances, which, by their combination, do not sensibly change their nature; but in this mixture, the nitric acid and the sulphuric acid must, while they preserve

preserve their constitution, be regarded as two simple substances.

When, by the action of a resulting force, the compound substance enters into a combination, the union of the elementary parts is strengthened by all the saturation it experiences from it; thus, iron, which can easily decompose nitric acid, is not capable of doing so when the latter is combined with pot-ash; and the oxygenated muriatic acid which yields its oxygen with such facility, retains it much more strongly in the oxygenated muriate of pot-ash.

The contrary effect takes place when, instead of a saturating substance, which serves as a support to the resulting affinity, a body is added which tends to form a combination into which one of the elementary parts must enter; for example, when sulphuric acid is added to a mixture of iron and water, this acid favours the decomposition of the water, because it tends, as well as the oxygen, to combine with the metal, and the decomposition of the water is determined by the union of their forces: those effects of affinity which have been called *predisposing*, consists in this union of forces.

The caloric which tends to restore the elasticity to condensed substances, at the same time weakens or destroys the union on which the resulting affinity depends, either by the sole effect of its action, or by the concurrence of other affinities; thus

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ters into combination with the particles of the charcoal is subject to the same conditions as if the oxigen gas had been immediately combined : all its superfluous caloric is eliminated in either circumstance ; the carbonic acid is invested with the same properties ; the elementary affinities have succeeded to the resulting affinity, or rather a new resulting affinity is established.

An inflammable substance will promote the decomposition of one which is oxygenated so much the more, as it has a greater tendency to combine with the oxigen, and as this is more feebly retained in its combination : it will therefore produce this effect more easily with the super-oxygenated muriate than with the nitrate of pot-ash : a very oxidable metal will require less heat than one which is but little so : and, finally, by the union of favourable circumstances, compression will be sufficient to produce decomposition.

190. If the difference which exists in the action of the same substance, according to the constitution it may have in the circumstance in which it exercises it, is not distinguished, inferences, very opposite to the laws of affinity, may be drawn from the observation of it: thus, in considering the action of liquids and solids, it is found that the action of a substance is diminished, in proportion as the quantity of it which combines with another is greater ; but if the attention is directed to sulphureous acid compared with sulphuric acid, it will be seen that although

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the sulphur is in greater proportion in the first, and, consequently, in conformity with the general theory, should retain the oxygen with more force than in the latter, it is nevertheless the contrary which takes place; for sulphurated hydrogen gas, iron, and several other metals decompose sulphureous acid by carrying off the oxygen, but they have no action on sulphuric acid, in the same circumstances of liquidity; so also nitrous gas yields its oxygen to metallic substances more easily than nitric acid.*

When elastic substances pass from a state of condensation to a state of dilatation, greater or less according to the combinations they form, they take other dispositions in these combinations. Their state produces effects opposite to those which are owing to condensation; this gives rise to the combinations which are determined by the circumstances, and which differ in the state of condensation, and in the proportions of the elementary parts: these different combinations, in consequence of their constitution, exercise an action which is as different from the preceding as if they had other constituent parts; thus laying aside the circumstances in which the sulphureous and sulphuric acids may be transformed into each other; they offer in their combinations, and in their habitudes, as great differences as two acids which have different elementary parts.

* Système des Conn. Chim. tom. vi. p. 350.

191. This diversity of phenomena comes under the general laws, if the effects of the elasticity which is opposed to the combinations, and which diminishes the quantity found within the sphere of activity, in respect of liquids and solids, which with the same volume can act in much greater quantity, are admitted among the causes which contribute to their production ; and, if the properties which a substance acquires by the condensation of its gazeous elements are distinguished from the saturation which these elements experience.

It is from not having considered these effects of elasticity, and of the disposition to elasticity, that they have been confounded with those of affinity, independent of the circumstances which modify it, and that it has been asserted that the acids, naturally elastic, possessed a weaker affinity than those which are more fixed ; in like manner it is from not having distinguished the effects arising from condensation, and from the capacity for saturation, which is the boundary of the action of the acids on the alkalis, that sulphureous acid has been considered as a much weaker acid than the sulphuric, notwithstanding that an equal quantity can saturate a greater quantity of an alkaline base ; in fine, from having neglected the consideration of the theory, consequences have been drawn from some observations which contradict those deduced from other observations.

Thus, although several facts prove that there is a greater

a greater disposition in hidrogen than in carbon to combine with oxigen at all temperatures, and although an equal weight of it produces a greater saturation in a greater quantity of oxigen, yet since it has been seen that the water which passes over charcoal, in a state of vapour, is decomposed by exposure to the action of heat, it has been concluded that carbon has a greater affinity for oxigen than hidrogen has. In this case there is an association of circumstances which share in the result: the hidrogen is disengaged to combine with the carbon, so that carburated hidrogen is formed, and it is not the hidrogen which is eliminated, and, at the same time, the oxigen combines with another part of the carbon; but carburated hidrogen and carbonic acid have both a great disposition to elasticity which increases as the temperature is raised, and the total of the dilatation to which they attain, is much greater than that of water.

Phosphorus decomposes sulphuric acid, but it does not decompose sulphureous acid; it has been concluded from this, that it could not decompose the sulphuric acid beyond a certain term; that the action of the sulphur, by becoming more powerful in proportion as the oxigen diminishes, then counterbalances the affinity of the phosphorus for the oxigen, and that in consequence the affinity of the first is greater; but the observations which I have detailed (190) have been lost sight of, and which prove that the oxigen abandons the sulphur more

more easily in sulphureous acid than in sulphuric acid. It is therefore only from those circumstances which depend on the force of cohesion of the phosphorus, and on the volatility of the sulphureous acid, that the phosphorus acts less on the sulphureous, than on the sulphuric acid, although the oxygen adheres more strongly to this latter: the heat requisite to diminish the force of cohesion of the phosphorus increases the elasticity of the sulphureous acid, so that it escapes from the action of the phosphorus, while other substances which exercise a much weaker action, can decompose it.

192. Thus, substances naturally elastic, have a disposition which leads to great differences in their action, according to the circumstances in which it is exercised; while they are retained in a combination, and only experience a condensation common to the other substances, they must be considered as similar to them, and the changes of dimension produce no influence on them but by the greater or less disposition to solidity; but as soon as their elasticity changes the constitution of the substance, their action is modified proportionally; heat, by this means, diminishes their resulting action; the substances which act on them by a resulting force contribute to maintain their state, and those whose action is directed to one of the elements of the combination rather than to another, concurs with the heat to destroy it: in this effect the elementary affinities supersede the resulting affinity,

SECTION

SECTION V.

Of the Limits of Combination.

CHAP. I.

Of the Proportions of the Elements in Combinations.

193. I HAVE examined the causes which produce the separation and insulation of combinations, and I have found them in the effects of solidity and elasticity; an interesting problem remains to be solved; it is to ascertain what are the dispositions and the circumstances which cause fixed proportions in certain combinations, while others are formed in all proportions; and what relations there are, in this respect, between the combinations which are formed by the agency of solidity, and those which are produced without losing the elastic state, and which preserve their properties and their proportions in the midst of other elastic fluids, while there are also some which can

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can receive variable proportions ; but with respect to these fixed combinations, it is still proper to examine what there is certain, or what may have been exaggerated in this property which is attributed to them.

Among the results of chemical action, there is none whose cause has been less attended to than that of the limitation of the proportions observed in some circumstances, while on other occasions the combinations are made in all proportions ; and that of the difference which is found, in this respect between the solids, the liquids and the elastic fluids.

When a compound was found more or less fixed in a certain number of combinations, it was considered as an attribute of the elective affinities to determine the proportions of the combinations they formed by the different energy of their action, and no inquiry was made as to what was positive in the constancy of the proportions ; how far this property really extended ; or what distinguished the chemical action of the bodies which possessed it, from that of the substances which were deprived of it.

Nevertheless it was observed that the effects of the tendency to combination are not always limited to these proportions, even in the saline substances in which the action of an energetic affinity is manifested ; in conformity with the ideas which had been adopted, it was then supposed that, in these cases, there were different terms of saturation ;

two, for example, as in the salts which can crystallize in a neutral state, or which can be acidulous; but it has been seen that combinations were formed in very varied proportions, and with regard to these, the law which chemical action follows, whose effect is greater as the quantity of the substance which exercises it is more considerable, was not wholly overlooked; sometimes a physical affinity, which acts in the ratio of the quantity of the substances, was distinguished from chemical affinity, to which an elective faculty of forming combinations of substances, which chuse or exclude each other, independently of the quantities which are in action, was attributed.

In fine, latterly, it has been found that the form of the moleculæ of a substance, or of the integrant parts of a combination, determined all the secondary forms which could be produced by their union; and it has been inferred that this primitive form determined the combinations themselves, and consequently the proportions of their elements.

I shall now endeavour to find the explanation of the different states of combination in those circumstances which vary the effect of the affinity which produces a reciprocal saturation of the tendencies to oombination, and to establish a better defined boundary than I have yet done, between its immediate effects, and those of the reciprocal action to which solidity is owing.

194. If we direct our attention to the phenomena

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mena offered by the weak combinations which produce solution, we observe that a solid body, a salt, for example, dissolves in all proportions in water, as far as the extreme term which produces saturation, and at which the dissolving force is weaker than the force of cohesion opposed to it; but that the degree of saturation varies according to the temperature which diminishes the resistance of the cohesion; a degree of temperature too much raised gives so much elastic tension to the water, that it abandons the salt which it held in solution.

The metals which alloy with each other dissolve in all proportions, when the difference of specific gravity and of fusibility do not interrupt this mutual solution.

Those substances which vitrify, also combine in all proportions, to the term, at which the insolubility of some of them, and the degree of temperature, produce an obstacle to this solution, which is uniform and transparent, and which consequently has all the characters of a chemical combination in which all the properties have become common.

The solution of an elastic substance by water offers analogous phenomena; the more considerable the quantity of the water is, the greater is the proportion of the elastic substance which dissolves: but heat, which promotes the solution of a salt, by diminishing the resistance of the cohesion,

sion, in this case produces a contrary effect, because it increases the elasticity which is the obstacle to the combination.

If now we put two combinations in opposition, we observe that the separations which may be produced are still an effect depending on the quantities which act, and of the resistance which the force of cohesion or the elasticity oppose to it: let water be well saturated with carbonic acid, the air will carry off more or less according to its quantity, and according to the temperature which will regulate the elastic effort of the carbonic acid: if, on the contrary, the air holds much carbonic acid in solution, water which is deprived of it, and which, consequently, possesses all its power, will abstract it to a certain extent; when its action ceases to be efficacious, lime water can take from the air that portion which it was capable of defending against the force of the water.

If ether is exposed to the action of the air, a part will take the elastic state, and will correspond to the volume which the air occupies, and to the temperature; but if it is then brought into contact with water, this will restore the ethereal vapour to the liquid state: it acts in the ratio of its quantity, and its power diminishes by saturation; for when it is arrived at an advanced stage of saturation, the air deprives it of some part, and the division is made according to the state of the forces, and, consequently, according to the degree

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degree of the elasticity determined by the temperature.

In these simple phenomena, of which it would be useless to accumulate a greater number, it is the affinity which produces the combinations, which only differ in intensity from those which are particularly considered as chemical; its procedure is shown without obscurity, and if, when it acts with more energy, the phenomena are not equally regular, it is doubtless because the circumstances which then accompany it, change the state of the forces which produce the result.

195. I have multiplied the proofs sufficiently to show that it is the essence of chemical action to increase in the ratio of the quantities of the substances which exercise it, and to produce combinations whose proportions are gradual from the first to the last term of saturation; but in a great number of combinations the proportions do not follow this progression, and separations are made which are owing to the participations determined by the elements of these combinations. The force of cohesion, or the elasticity, become preponderant to produce these separations; but it is not enough to collect these results from the observation of each particular case, the dispositions and circumstances on which these properties may depend, and which sometimes render the effect uniform, while on other occasions they do not observe it, or do not appear to be subject to any regularity, must be examined.

Kirwan

Kirwan has examined the specific gravities of sulphuric acid and nitric acid, mixed with different proportions of water, and he observed not only that they were greater than should have resulted from the specific gravities of the two liquids separate, but also that there was one proportion in which they were greater than in the others.

Experience therefore shows, that in combinations there is a proportion of the substances which form them, in which their action has the greatest effect, and at which their mutual affinity is exercised with the greatest advantage, with respect to the condensation : it must be obvious that it is in these proportions that the force of cohesion acquires the most considerable increase, and that the elastic combinations receive the greatest density : but this conclusion supposes an equality of dispositions in the substances in which the condensation takes place.

When the action is exercised between two liquids which can only experience a certain degree of condensation, that does not produce any separation, two terms are observed at which the effect of the condensation is greatest ; the one, when one of the two liquids predominates by its quantity ; the other, that in which the second liquid is in the greatest proportion : this is shown in the observations of Blagden on the mixtures of alcohol and water, with a view to ascertain, by their specific gravities, the proportions of the two liquids in

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in brandy :* it results from his experiments, made with great care on increasing proportions of alcohol with 100 parts of water, and on proportions of water mixed successively with 100 parts of alcohol, that it is by the mixture of about 15 to 20 parts of one of the liquids with 100 of the other, that the greatest effect of condensation is produced by the addition of one liquid to the other.

Thus, the theory which I have proposed on the force of the affinity, which increases in the ratio of the quantity with which a substance can act, must be modified with respect to condensation, because this effect not only depends on the action which it exercises, but also on that which it experiences ; and it is in certain proportions which are very variable according to the dispositions of the two substances which exercise a mutual action, that this effect is greatest : in those liquids whose state is not changed by this action, there are two terms at which the greatest condensation takes place ; nevertheless, a perfect equality in the dispositions of each of the liquids must be supposed, for the quantity of the condensation to be equal in both, so that it may be advanced, generally, that in the chemical action of two liquid substances, there is one proportion in which the greatest effect of the condensation is found.

This term of the greatest condensation experienced by liquids, must be that at which they are

* Philos. Trans. 1792.

the most disposed to congeal, or to take the solid state, since solidity is itself the effect of a condensation of the moleculæ, which then exercise their reciprocal action with more energy: this will explain some observations of Cavendish and Keir.

Cavendish observed, that when a mixture of acid and water was submitted to a great degree of cold, if the latter was in too great proportion, part of it congealed and separated; that when this separation had arrived at a certain degree, the mixture itself remained in congelation, so that he distinguished the aqueous congelation and the spirituous congelation: he remarked that this latter took place with greater facility, in certain proportions of water than in others, so that the greatest disposition of an acid to congeal is not at the greatest point of its concentration.

Keir confirmed these observations of Cavendish;* he showed that there is a term of concentration in sulphuric acid at which it possesses the property of congealing in the highest degree, and that this term is nearly that at which its specific gravity is 1800, so that, above and below this gravity, its congelation requires a greater degree of cold.

Nevertheless, the condensation which belongs to the proportions can only have a greater or less share in the preceding facts, because the disposi-

* Philos. Trans. 1787.

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tion to congelation may be very unequal in the two liquids which are mixed, and because their combination is too weak to counterbalance the effect of the reduction of the temperature, so that the congelation may be able, for example, to separate a part of the water mixed with the alcohol, which will differ greatly from the proportion at which the condensation is the greatest when the water predominates: it may perhaps also exceed the proportion of the greatest condensation produced by the predominancy of the alcohol; because at this term the effect is compounded both of that which the cold produces on the alcohol, and of that which it produces on the water: this is not the case with sulphuric acid, which has a sufficiently great disposition to congeal: the separation of the water will also go beyond the first term, but it is probable that it will stop, nearly, at the last.

The effects of condensation are, therefore, complicated in those substances which are only retained by a feeble combination, and which can yield to a cause which has but little efficacy for its separation; but they must be much more uniform when the combination is more energetic, and when no change in the state of the saturation is produced by the condensation.

196. If, in liquids which exercise only a slight reciprocal action, it be observed, that the condensation which results from it is greater in certain proportions than in others, this effect must
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more particularly take place in those combinations which are produced by a strong affinity, such as the saline combinations; but the dispositions which are found in each of the elements of the combination may contribute unequally to the separation which a greater condensation can produce; so that it is not the greater condensation alone which can determine the spontaneous separations of the combinations, but this effect may also depend on the dispositions of their elements, and on the circumstances which give more influence to one cause than to another.

If the condensation increases the force of cohesion, or the reciprocal action of the molecule, the combination which is separated from this cause resists a contrary action, by all the augmentation of force produced by the approximation of its particles; so that a species of interruption is introduced into the progress of the chemical action, similar to that which is found, in an opposite action, in the thermometric effects of heat, while it accumulates in a body which is passing from the solid to the liquid state, or from this to an elastic state. This resistance will be so much the more considerable, as the force of cohesion acquired shall be greater; but as soon as it is overcome, the laws of chemical action will resume their full effect, that is to say, the action of all the substances will be proportionate to their mass.

The cause which produces the separation of a
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substance which acquires the solid state, is therefore also that of the proportions in which it separates : these proportions are those in which the force of cohesion has sufficient energy to produce the separation: they must be uniform when the circumstances are the same, or when the effect of the condensation is superior to that which they can produce, as water congeals at nearly the same degree of temperature, when the chemical action of some substance is not opposed to it: in this state the combination resists the chemical action until it has acquired an increase which is more considerable than the effect of the condensation. The general law of affinity is only apparently interrupted, because an obstacle which arises from its own action opposes the progress of its effects until it has acquired sufficient force to overcome it.

197. Since the force by which a combination is formed produces a condensation, and by that means augments the effects of the reciprocal action, it must result from thence that these effects will take place more particularly at the term of saturation at which the two elements of the combination exercise the greatest degree of their power, if both possess an equal disposition to solidity, or if one cause produces an equivalent effect on both; but if one of the two has naturally a greater disposition to solidity than the other, it is the excess of this which leads to the separation of the compound. In those combina-

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tions whose elements appear to have nearly equal dispositions to solidity, such as the salts with base of soda, of pot-ash, and of ammonia, and whose acids are the muriatic, nitric, and acetic, the greatest degree of concentration must consequently be at the term of neutralization; and that which confirms it is the disengagement of heat, which is an effect of this condensation: for if these neutral salts are dissolved in an excess of acid, although deprived of the water of crystallization, either cold is produced, as with the muriate of ammonia, or only very little heat is disengaged, and incomparably less than when the combination is stopped at the state of neutralization, so that the liquefaction produces a dilatation of volume which overcomes the effect of the condensation arising from the combination, and which shows that, beyond the neutral state, this condensation is much weaker.

The combinations, whose elements have nearly an equal disposition, separate therefore in the neutral state by crystallization, because it is at this term that the condensation is greatest; but the insolubility will be so much the more considerable, the reciprocal action being supposed to be but little different, as the elements of the combination shall have a greater disposition to this property: thus the phosphoric, oxalic, tartarous, and sulphuric acids, must easily produce insoluble salts with earthy bases; on the contrary, the muriatic, nitric, and acetic, must form much more soluble

ones: nevertheless, the influence of the capacity for saturation may show itself in these effects; thus, magnesia and lime, which differ much more in this respect from barites and strontian, than the muriatic and nitric acids from each other, must act much less by their disposition to solidity, than barites and strontian; nor can it even be surprising that they form deliquescent salts with these two first acids, while pot-ash itself and soda produce salts which crystallize, since less of these earths enter into combination.

Thus we find in the properties of salts formed by the alkaline bases with the acids, an exact correspondence with the supposition that their insolubility depends on the natural disposition of their elements, increased by the condensation arising from the affinity which unites them: explanations, which may have the appearance of being doubtful, are not required, except with respect to the formation of some deliquescent salts, which have nevertheless an earthy base endowed with great solidity; but these explanations are supported by a consideration of the precipitates which the combinations themselves yield, as soon as the action of their acid diminishes.

198. The force of cohesion peculiar to the elements of the combination is to be considered as a latent property, which either retains a sensible influence, or resumes it when the force which had rendered it imperceptible diminishes, as we have seen in the reciprocal action of acidity and alkalinity;

linity; and in some cases, it acquires a new energy which is owing to the condensation: in fact the earthy alkalis, which are in themselves but slightly soluble, easily form combinations of the same description, or, when, by the influence of the acid and of its quantity, their combinations are soluble, they lose their solubility if the quantity of the acid is diminished, or what amounts to the same thing, if its action is weakened by being divided: hence arise the precipitates which take place when another alkaline base participates in their action on the acid which rendered them soluble.

These precipitates are therefore to be considered as combinations which have an excess of alkali, because the insolubility peculiar to these alkalis produces their separation when it becomes preponderant; it is but seldom that this species of combination can be immediately produced, because the force of cohesion occasions too great an obstacle: I shall nevertheless give an example, and if the attention is directed to this point, others will doubtless be discovered; the metallic salts also offer several facts of this description.

Bucholz obtained beautiful crystals by boiling lime with its muriate: Trommsdorff has verified this fact*; to obtain these crystals, he directs a quantity of muriate of lime to be boiled with a quarter, or less, of caustic lime; the long selen-

* Journ. de Chim. de Van Mons. No. 2.

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der crystals which are formed are to be purified by alcohol.

I have repeated this experiment and have ascertained that these crystals are not lime, as has been announced, but a muriate of lime with an excess of lime; if these crystals are treated with water other proportions are established; the part which is dissolved is the muriate which retains but little of the excess of lime, and that portion which does not dissolve retains a greater excess of lime: successive separations may be obtained by additions of water, and the proportions which are produced depend on the relation of the dissolving force with the resistance of the force of cohesion.

199 The acids which have a considerable force of cohesion, offer phenomena which are analogous, or which manifest no other difference but that which proceeds from their greater solubility; on this quality depends the property possessed by the tartarous and oxalic acids, of forming combinations with an excess of acid with bases of great solubility, which are much less soluble than their neutral combinations, and which are indebted to this insolubility for their existence, while with bases but slightly soluble they form, immediately, neutral combinations: in this case the insolubility is attached to an excess of acid, as it is in the preceding circumstance to an excess of alkali: by the addition of a soluble alkali, the solubility is augmented,

augmented, and, by crystallization, a salt is obtained which is also more soluble; but an alkali which is but little soluble produces a contrary effect, and a precipitate is formed.

Hence it is evident why acidulous salts are only formed with those acids which show a considerable force of cohesion; it may also be remarked that this property is united with that of forming insoluble salts with those alkaline bases which are but little soluble in themselves, and which are designated earthy. The acids which in themselves are but little disposed to cohesion, have therefore a tendency to form soluble combinations; and it is the same with alkalis; they both produce insoluble combinations when they have a great disposition to solidity; but the effects of these dispositions combine when the acid and alkali are united.

In fact, ammonia never produces an insoluble salt, when its quantity is alone sufficient to give the neutral state to an acid; it is the same with soda and pot-ash: but lime, barites, and strontian, have, more especially, the property of forming insoluble salts.

Hence the theory of precipitations is brought to that of the determination of the proportions in combinations; when a precipitate is formed, all that takes place is a change in the proportions, by which the insolubility of a substance, which had been concealed by the action of another, whose power

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power was sufficient to produce this effect, but which ceases to be so, is rendered predominant.

The degree of solubility peculiar to acids does not correspond exactly with the property which they possess of becoming solids by evaporation, or by congelation, because the affinity which they have for water is capable of diminishing the effect of their disposition to take the solid state; thus phosphoric acid, which easily quits the water it contains to pass to a solid state, nevertheless, in some combinations, announces a disposition to solidity, which is even inferior to that of sulphuric acid: it is, therefore, rather by the properties which acids have in their combinations, that a judgment can be formed of their disposition to solidity.

I am far from pretending that in the comparison of the phenomena which I analyse, there may not be some which do not answer to the conditions I assign to them; but in the explanation of phenomena to which a great number of properties contribute, we must not expect to be able to determine all the causes which act, and which may lead to modifications in the results: the number and the agreement of these results may, however, be sufficiently great to show the principles from which they are derived, particularly when they are established on general principles which cannot be controverted, and which have the advantage of connecting phenomena with these general principles,

ciples, which appeared to be independent of them.

It is only by separating in this manner the properties which contribute to the same phenomena that we succeed in distinguishing the effects of caloric and of other physical causes, and in establishing a theory founded on their mutual dependence.

200. If the preceding observations prove that the force of cohesion determines the proportions of many combinations to the degree of neutralization, at which the mutual action produces its greatest effect, or to some other degree of saturation according to the superior dispositions of one of the constituent parts, it must not be concluded that combinations of the same elements, in other proportions, cannot exist, which may be influenced to separate by an inferior degree of the force of cohesion, or that if this takes place, it must still be in fixed proportions, so that there could be neither separation nor crystallization but in the one or the other proportion. This opinion, which is applied to many combinations, and which has been almost received as a general law, has been particularly grounded on the consideration of the acidulous sulphate of pot-ash and of the acidulous phosphate of lime: I shall examine what relates to these salts, and to some others; until I can direct my observations to a greater number of analogous combinations.

Bergman explained the decomposition of sulphate

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phate of pot-ash, by nitric acid, first observed by Beaumé, by considering the sulphate as composed of two parts, one of which had the proportions of an acidulous sulphate, and the other of which was the portion of pot-ash which reduced the acidulous sulphate to neutral sulphate: the acid only exercised a part of its force on this latter, because the other part was exhausted by the acidulous sulphate, so that a much weaker acid than the sulphuric could carry off the portion of the pot-ash which was partly free, by separating it from the acidulous sulphate; but this was the limit of the decomposition which was possible, and the salt passed at once from the one to the other term of saturation, and could not receive other proportions. In proving, in my Researches into the laws of affinity, that it was contrary to observation to pretend that the action of the sulphuric acid was confined to the term which forms the acidulous sulphate, and that it might be prolonged indefinitely by a progressive loss of its intensity, I retained the erroneous opinion that this acidulous sulphate was a uniform combination; determined by a force of cohesion peculiar to the figure which I had supposed to belong to certain proportions.

201. I have examined this subject again, and have observed that the acidulous sulphate of pot-ash might receive different proportions of acid in excess, from the neutral state to that in which the solubility, which becomes greater and greater, will not permit it to separate from the liquid acid
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in which it is formed ; so that I was convinced that the supposition I had admitted ought to be rejected, and that the ingenious explanation of Bergman was only imaginary.

An acidulous sulphate of pot-ash was dissolved in a certain quantity of water, and after a suitable evaporation submitted to crystallization, new crystals were formed a little less soluble than the first : the liquid was again evaporated, a sulphate more acid and more soluble crystallized : several successive crystallizations were made, and in each operation a division took place; the salt which crystallized first had a little less acid than that from which it separated ; that, on the contrary, which remained in solution gave, by evaporation, another salt, which had a greater excess of acid, and the properties belonging to these proportions ; each solution separated by a suitable evaporation into two combinations. At length nothing was obtained but the perfectly neutral sulphate, but the intermediate states between this and the first acidulous sulphate depend only on the circumstances of each crystallization. The proportions of acid in four acidulous sulphates, obtained by the first crystallization of the four last operations, were compared, by decomposing equal quantities of each with acetite of lead ; the precipitate obtained from that which was reduced to the perfectly neutral state weighed 30.2, that which immediately preceded it 32.4, the third in this order 33.3, and the fourth nearly 35.

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The form of the crystals experienced several variations, but their changes did not follow those of the proportions of the acid: thus, the salt resumes the form of the sulphate, although it still preserves a certain excess of acid.

The acidulous sulphate of soda offered analogous properties: it forms large crystals perfectly similar to those of the neutral sulphate, although it contains a pretty considerable excess of acid; these crystals effloresced, but less rapidly than those of the neutral sulphate: with a greater excess of acid, the crystals take a different form, and are maintained in the air without efflorescence: the neutral salt only contained half as much acid as that which had retained the greatest quantity, and which did not deliquesce or effloresce.

202. It has been observed, that, after having decomposed the osseous matter by phosphoric acid, a deposition was formed by evaporation, which was confounded with sulphate of lime. Bonvoisin proved,* that it was phosphate of lime; but Fourcroy and Vauquelin have shown† that this substance was an acidulous phosphate: they considered it as a combination whose proportions were not variable, since they determined them at 54 of acid and 46 of lime, and those of the neutral phosphate at 41 of acid and 59 of lime.

* Mém. de Turin, 1785.

† Mém. de l'Instit. tom II.

This acidulous phosphate was formed that it might be submitted to an examination similar to that of the acidulous sulphates.

Water did not dissolve it, as was announced by my learned colleagues; but it caused a separation: it dissolved a more acid phosphate, and the residuum was insoluble, but with a less proportion of acid; by several washings, which also produced similar separations, it no longer retained any excess of acid. Since the acidulous phosphate of lime, as this experiment proves, may contain different proportions of the acid, it is probable that that employed in my trials contained less acid than that which was analysed by Fourcroy and Vauquelin. (*Note XIII.*)

Alcohol separated the greatest part of the excess of the acid from the acidulous phosphate, which retained only a small part of the lime; but it was unable to deprive it entirely of this excess; water at length completed the separation.

If a great proportion of alcohol is poured at once over the acidulous phosphate of lime, it takes the phosphoric acid, which only retains a little of the lime; but if only a small proportion of alcohol is employed, it then dissolves much more of the lime, because the acid being more concentrated can act more efficaciously on this base.

It is therefore ascertained, that the acidulous phosphate of lime contains an excess of acid differing according to the circumstances: in fact, Fourcroy and Vauquelin themselves say, that having

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having poured sulphuric acid over a solution of acidulous phosphate of lime, obtained from bones by the muriatic or nitric acid, sulphate of lime was precipitated, whence they concluded that sulphuric acid could deprive the phosphoric acid of a greater quantity of lime than the other two acids. A great number of other circumstances may also cause a variation in the proportions which take place in the acidulous phosphate, which consequently can only be regarded as the variable result of an affinity which is in competition with those opposed to it.

The properties of the acidulous phosphate of lime are therefore perfectly analogous with those of the acidulous sulphates of pot-ash and of soda, and the difference which exists between these salts only consists in the insolubility which becomes proportionably greater in the acidulous phosphate of lime, than in the acidulous sulphates; so that if it undergoes a sufficient number of washings, a division of the combinations more or less acid will be obtained, while in the sulphates this effect can only be produced by repeated crystallizations.

203. Thus it is evident to what this theory of two terms of crystallization, in one of which a salt is neuter, and in the other has another proportion of acid, but equally fixed, is reduced: far from these two terms being the only ones, all the intermediate degrees between them can exist, and the properties, particularly the solubility, follow these

these proportions: the farther it is removed from the neutral state, the more its insolubility diminishes, because it is in that state that the effect of the affinity is greatest: but in the acidulous phosphate two causes concur to augment the insolubility; the force of the affinity of the lime which increases in proportion as the quantity of the phosphoric acid diminishes, and the preponderance of its force of cohesion, which also increases for the same reason.

The sulphate of barites also offers similar properties. Withering observed,* that crystals were formed when a solution of it was made in very concentrated sulphuric acid, by means of ebullition, by leaving this solution exposed to the air. I repeated this experiment, and noticed that the crystallization was formed in proportion as the acid attracted the humidity; the liquor was decanted, and the crystals, which were not very distinct, were washed in successive quantities of alcohol: they were even submitted to ebullition in this liquid, which afterwards, on being tried with a solution of nitrate of barites, gave but feeble indications of sulphuric acid; but the water with which it was then treated, gave an abundant precipitate with the same solution. These crystals were therefore an acidulous sulphate of barites: alcohol was incapable of carrying off more than a part of the sulphuric acid; but water acted with

* Philos. Trans. 1784.

more energy: I am satisfied that the sulphuric acid which it had taken did not retain any barites; but I did not ascertain, whether several washings were necessary to reduce this acidulous sulphate to the neutral state, or whether a great quantity of water was required to produce this effect.

204. These observations should guard analysts against the errors which may result from different proportions, either in the precipitates, or even in the salts which they obtain by crystallization.

We have just seen that sulphate of barites itself may have an excess of acid, but the sulphates of pot-ash and soda can retain it in excess in their crystallizations with much more facility, and even without any change in their form: these differences in the proportions are more particularly remarkable in the combinations of the phosphoric acid, which appears to me to depend on its great capacity for saturation, and consequently on the strong action it exercises; as the property possessed by ammonia and magnesia of forming triple salts without difficulty, appears to depend on the same cause. Klaproth has shown, that phosphate of soda may crystallize with an excess of acid; nevertheless it tends to an excess of base; and Thenard has proved,* that it could crystallize in this state, in a liquid slightly acid. When a phosphate of lime, held in solution by an excess of acid, is precipitated, by means of ammonia, the

* Ann. de Chim. Fruct. An. 9.

salt obtained by crystallization is a triple salt which contains a certain proportion of lime; but if a carbonate of ammonia is employed in the precipitation, the phosphate obtained has a smaller proportion of lime, and these salts, particularly the latter, cannot be distinguished by the form of their crystals, and by their other appearances, from that which is only composed of ammonia and phosphoric acid.

205. We have only considered the effects which arise from the contraction of the volume of the elements of a combination, and which produce a force of cohesion in the compound, greater than that of the elements; but we have noticed, (30), that the mutual action of salts increases their solubility: some combinations have more disposition to liquidity than the substances of which they are composed have separately; such are sulphur and phosphorus, which by their union acquire much fusibility, as has been shown by Pelletier: * these facts may seem contradictory.

Two causes, one of which is sometimes superior to the other, must be distinguished here, as I have done with respect to the caloric disengaged in combinations: when two substances act on each other, their reciprocal action diminishes the effect of the mutual affinity of the molecule of each of the substances by all the force which it exercises, so that it will make all the combinations

* Mém. de Chim. tom I.

more soluble than they are naturally, if the condensation, which is a necessary consequence of the combination itself, does not annihilate this effect, and produce an opposite one: when this second cause has not sufficient energy, the effects of the first predominate; it is thus that an augmentation of solubility is to be found in weak combinations, such as those which are owing to the mutual action of salts.

The effect arising from the greater condensation disappears whenever the action of caloric introduces a sufficient distance between the moleculæ, and this is confirmed by experience. When a combination is separated from a liquid by the force of cohesion which it has acquired, if the temperature is sufficiently raised, it shows a disposition to liquidity greater than the mean of the liquidities of the separate elementary substances; thus the muriate of silver, which is precipitated from a liquid, enters into fusion at a low degree of heat, although it contains but a small proportion of acid: sulphate of barites, which does not vitrify but at a high temperature, acquires a much greater fusibility from the action of the muriate of lime, from which it was separated in a liquid state: in the same manner the liquefaction of carbonate of lime is considerably promoted by sulphate of soda. (*Note I.*)

It is because the effects of the reciprocal action, which produces the force of cohesion, are thus diminished by the action of the moleculæ of another

other substance, that metallic alloys acquire a fusibility greater than that of the metals of which they are composed, although they may be harder and more elastic at an ordinary temperature, a property arising from the condensation, but which gives place to a greater fusibility as soon as the cause of it is destroyed: it is for the same reason, that earths which are infusible alone, acquire fusibility by mixture, and that the fluxes act, not only by communicating a proportionate part of their fusibility, but more especially by diminishing the reciprocal action of the moleculeæ of the substance whose fusion they accelerate.

It is therefore only by an exception, which arises from the weakness of their action, that some substances can augment the mean solubility, at a low temperature; they then act as solvents which increase the bulk of salts in a crystallized state, by causing the effect of the reciprocal affinity of their integrant particles to disappear; but as soon as the elevation of the temperature tends to destroy the effect arising from the approximation of the particles, the mutual affinity concurs with the action of the caloric and increases the effect; it is thus that a liquid dissolves a salt in greater quantity by the assistance of heat.

206. The effects of the reciprocal action which produces combinations are more considerable in gazeous substances than in others, because, in them, the changes of dimensions produced by the same force are much greater. Let us now ex-

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mine the uniformity and distinctive characters of the combinations which they form with respect to the proportions of the elements; a property which we have already considered under other points of view.

We have seen that the elastic fluids exercised a reciprocal action, even when their force was insufficient to bring about any change in their dimensions, (157); that then, only a weak combination was produced, which we have considered as a solution; but when they were able to act on their respective dimensions they formed a combination, and exercised a resulting affinity while it was maintained.

The quantity of the condensation, although it cannot be considered as commensurate of the chemical action, must nevertheless be considered as an index of it, and produces different properties in combinations.

When circumstances increase the mutual action of elastic substances, and when their combination is decided, they will unite in the proportions in which their action has the greatest force, (197); they will therefore take more uniform proportions than the other combinations, because the contraction, which is much greater in elastic fluids than in liquid substances, will occasion a much greater obstacle to the establishment of other proportions: we shall not therefore find, in the elastic combinations, which are accompanied by a great condensation, progressive combinations, similar to those

those of the acidulous salts which we have examined; but they will at once pass into combinations whose proportions are uniform, or which admit of but very small variations.

In this case condensation produces the same effect as the increase of the force of cohesion in liquid combinations: the greater the condensation is, the more it insulates the combination, as is done by the force of cohesion in precipitations; and when a combination is formed, it is maintained until the forces opposed to it overcome the affinity which produced the condensation, (196).

207. It will be seen, therefore, how oxygen and hydrogen, which, while they were in simple solution, and consequently retained the same volume, possessing, at the same time, their insulated properties, pass at once to the state of water, as soon as they enter into combination, and, by that means, experience a diminution of their dimensions, by separating from what is superfluous in the proportions at which they exercise the greatest action, or at least by only taking from each of the elements a small quantity which may be subdued by the action of the water, but which, by not experiencing the same condensation may be separated by a much weaker cause.

The condensation of the elements is such, that the mixture of oxygen gas and hydrogen gas, whose specific gravity should be 19.47, that of the air being 46, forms an elastic vapour which has a specific gravity of 33; but the action of the calorific,

ric, to which this state of vapour is owing, is so little energetic, that it only produces a weak elastic tension, and abandons it by a slight pressure, so that the specific gravity of this gaseous substance becomes a thousand times less at a similar temperature.

Ammonia is likewise composed of two elastic elements which have undergone a great condensation; for when ammoniacal gas is decomposed by means of the electric spark, it acquires dimensions nearly double: ammonia also has uniform proportions.

On the contrary, nitrous gas, in which the elements have only undergone a weak contraction, can easily form other combinations; by simple contact it combines with oxygen gas which has a tendency to unite with it in the proportions in which the respective action produces the most effect: but it experiences a much greater contraction from the action of water, and by its means forms nitric acid.

Although nitrous gas is composed of elements but little condensed; although it forms other combinations with great facility, and yields its oxygen to substances which are not very energetic, it nevertheless resists the action of heat which tends to separate its elements, and it appears that the feeble contraction of its elements serves to maintain its combination, because the heat produces but very little difference in the elastic effort which tends to separate them.

208. I shall now apply these considerations to the properties of a combination in which a gaseous substance is condensed, and a solid substance takes the elastic state: all the others offer analogous properties.

Sulphur, at a temperature but little elevated, combines with oxygen, until the term at which, in a fixed state, its action is not sufficient to overcome the force of the elasticity. Thus far it appears to take proportions which augment progressively, because the condensation it experiences is so weak that it does not sensibly change the state of its action, and also that there is no difference in the state of the condensation of the oxygen which is fixed.

If, instead of leaving the sulphur at a temperature at which this combination can be effected, it is reduced to vapour, it passes at once to that degree of saturation which forms sulphureous acid, the elements of which already experience a considerable degree of condensation with respect to the expansion peculiar to them at this temperature; in this state they oppose a tolerably great resistance to changes, and consequently even to the action of oxygen gas: if the temperature is not further raised, all the effect of this condensation must be overcome to enable it to pass to another state of combination; but if the temperature is sufficiently raised wholly to overcome the effect of this condensation, the reciprocal affinity of the oxygen and the sulphur will continue to receive its effect,

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effect, and it will produce sulphuric acid in the proportions of the two components in which this effect has the greatest intensity: but beyond that it is weakened, and can no longer contend with the resistance of the elasticity of the oxigen gas which continues to be increased by the high temperature which is necessary.

It is therefore at the term of the greatest effect of the reciprocal action that the sulphuric acid is formed; it is at this term that the condensation is greatest with respect to the temperature; and that the combination is the most energetic; a proof of it is, that this is the state in which it retains the oxigen with the greatest force.

A higher degree of heat, which would counterbalance the effect of this condensation by the dilatation, would destroy the acid by the increase it would give to the elasticity of the oxigen compared with that of the sulphur.

If oxigen has become condensed in a combination which nevertheless only retains it by a weak affinity, and if the sulphur on its part does not oppose a resistance of cohesion, as in the sulphurets, the oxigen may attain the state in which the greatest action is exercised at a low temperature, without the sulphur passing through the gradation of sulphureous acid.

When a sulphite is exposed to the action of fire, that effect of the condensation which maintained the sulphureous acid is destroyed; it then passes
to

to the degree of combination in which the greatest action is exercised, and the sulphite becomes a sulphate.

209. I shall apply to this case, that which observation has shown more distinctly in the crystallization of salts which can exist in an acidulous state; they take an excess of acid in one circumstance; they crystallize in a neutral state, when the strongest action which their elements can exercise does not experience a resistance which opposes this effect: in the present case, the oxygen combines at the term of the greatest action, if the state of the sulphur and its own state permit it; when it cannot accomplish this combination, it forms another: but as there are salts whose force of cohesion is such that they separate in proportions nearly uniform, there are also elastic combinations whose proportions are invariable.

If, therefore, heat assists the combination of a solid substance with an elastic fluid by diminishing the resistance of the cohesion, (156), it produces different effects, with respect to the proportions, according to its intensity, and according to the state of the vapour which it produces.

There can be no doubt that, in the circumstances in which heat produces combinations of elastic substances, which could not have been formed at a lower temperature, it only acts by bringing the substances into that condition in which their strongest affinity can be exercised, if we consider that it will be sufficient to destroy the force

force of cohesion to enable the same combinations to be effected at a lower temperature: it requires a very powerful heat to combine silver with copper, but if muriate of silver is employed, it alloys with the copper by a slender friction; nevertheless the combination which it had formed with the oxygen and muriatic acid was an obstacle to another combination, but the separation of its particles overcomes the effect of this combination, and it alloys with the copper without the assistance of heat.

Besides, heat will obstruct the combination of elastic substances by all the tension which it communicates to their elements; but the effect which it produces, by the dispositions it occasions in the substances which combine together, is superior to this cause of separation: nevertheless, by too much intensity, it decomposes combinations, whose production it had occasioned, and it is thus that it destroys the resulting affinity, and that, by that means, the elementary affinities succeed to it, (184).

210. To return to what I have laid down in this chapter, we must distinguish that which is common to all combinations; that which belongs to solid, liquid, or elastic combinations; and, finally, that which is peculiar to their passage from one state to the other.

1st. Combinations which experience but little condensation, may take place in all proportions; they are only limited by saturation, that is to say,
by

by the diminution of the action which overcomes either the force of cohesion, or the difference of specific gravity, or any other force which may oppose it: thus alloys, glasses, mineral combinations, are made in very variable proportions, and in which the interruptions occasioned by the resistance arising from condensation are rarely perceived: salts unite with water in all proportions as far as saturation.

2d. When an obstacle opposes the continued progression of a combination, and requires that an accumulation of force should be obtained, the moment it is overcome, the combination takes, at once, all the quantity and the properties which it would have acquired if the progression had been continued: thus, by ebullition, water gains all the caloric which corresponds with the state of vapour.

This obstacle is in the force of cohesion, in those combinations which separate because they are insoluble; but they do not always take the proportions of the greatest insolubility: they may have an excess of either element, according to the quantities which can exercise their action, so that there is but a small number of insoluble combinations whose proportions are constant.

3d. To produce a separation, the force of cohesion, arising from the reciprocal action, must be greater than the diminution of cohesion peculiar to each element which results from the same reciprocal action: but the effect of the condensation

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tion ceases to operate by the separation of the moleculæ caused by the caloric, so that the combinations which were separated by insolubility, become afterwards more soluble, by means of the reciprocal action of their elements. It is because the affinity of the water overcomes the reciprocal affinity of a salt, which it dissolves, and because the concentration produced by this combination is weaker than that which existed in the solid body, that an augmentation of volume is made in the solution, and that it is accompanied by the production of cold: but this effect can only take place with weak combinations.

In a weak combination, therefore, we must distinguish the effect of condensation from that which is due to the reciprocal affinity of two substances; the first increases the force of cohesion; the second diminishes that which belonged to the elements of the substance, before combination: if the first is weak, the second bears sway; and hence arise the combinations whose solubility is greater than that of the separate substances.

4th. In the reciprocal action of elastic substances, the effects of the condensation may be much more considerable: from hence it arises, that they frequently form combinations whose proportions are uniform. Nevertheless, when the reciprocal action is not strong, and does not produce too great a difference in the condensation, these proportions may differ considerably; thus,

the

the carburated hidrogen, oxicarburated, sulphurated hidrogen, and phosphurated hidrogen gases can have very different proportions.

211. When an elastic fluid is condensed in a combination, it then forms a particular substance, which acts like a simple substance while the causes which have produced the combination are not destroyed; thus, this combination may be held in solution, or be sur-compounded, either with elastic fluids, or with liquids, or with solids.

The combinations of an elastic fluid may, therefore, like the others, either take place in all proportions, or it may meet with obstacles which restrain it more or less: if a combination of two gases is formed, and if they exercise a reciprocal action sufficiently powerful to change their respective dimensions, it takes those proportions which are fixed by the term at which the action is strongest: if the combination is that of a gas with a liquid, the proportions seem to be limited only by the resistance of the elasticity, because, by dissolving, the elastic fluid is reduced to a state nearly uniform; in the same manner, if a liquid is dissolved by an elastic fluid, there is no other limit but that of the constitution of the liquid which has taken the elastic form, because in this state another gas cannot change its dimensions but by a common compression.

When an elastic fluid enters into combination with a solid substance, it is so much the more condensed as the action it experiences is stronger,
and

affinity so powerful, that it excludes a great quantity of the caloric which each contained, and that they form a new combination in which their elasticity is considerably diminished, and their properties experience a saturation more or less complete.

Liquids themselves show but weak traces of the force which produces cohesion: nothing more is required but to diminish the pressure they experience, and they take the elastic state of themselves, nevertheless, they possess all the activity of the affinity which produces combinations.

From this I conclude, that affinity, as a principle of combination, has a much greater extent of action than the force of cohesion; that the reciprocal action of the moleculæ which produces this, is, in combinations, no more than a consequence of the first; that it can have but a weak influence in them; and that, consequently, the figure of these moleculæ is nearly foreign to the effects of the affinity which produces them.

Can it be believed, supposing that the moleculæ of oxygen gas and hidrogen gas have a figure which is peculiar to them, that it has any influence on the formation of water, while in this, which is nearly two thousand times more condensed, the form of the moleculæ does not begin to be manifest, or to produce sensible effects, until it experiences a new condensation?

It is only when the integrant parts of a combination have acquired a sufficient approximation,
that

that they begin to exercise a mutual action whose effect augments in proportion as the approximation becomes greater: thus gravitation affects all bodies, and it is only very considerable masses which can sensibly modify its effect in small bodies which are near each other.

It is even probable, that when the moleculæ are far distant they have no determinate figure, but that, obeying the expansive action of caloric, they take that occasioned by an effort which acts in every direction: for the same reason, the phenomena which may be attributed to a peculiar figure in the moleculæ is never observed in elastic fluids, and very seldom in liquids. It seems, that they do not take a determinate form, except when, by an effect of affinity, they undergo a condensation, or, without changing the state of saturation, they are influenced by the effort which brings them together, and by the resistance of their caloric which opposes its effect.

The form which the integrant moleculæ then receive can only contribute to the chemical properties by as much as it increases or diminishes the specific gravity, or even the cohesion: when a precipitation is formed in an earthy or metallic solution, the quantity and the properties of this precipitate are independent of the circumstances which might favour the mutual action of the moleculæ on account of their form; the force of cohesion is produced, but the figure has not yet acquired any influence on the properties of the

detached integrant molecule; it is only when they can mutually exercise a tranquil and slow action, that this figure can determine that of the groups which are formed. At that point the phenomena of crystallization commences.

Newton, with that discernment which is found in all his enquiries, has pointed out the distinction of the phenomena arising from the affinity which produces combinations, and from that by which their molecule take the symmetrical arrangement of crystallization.

After having described the effects of the affinity which produces several combinations, he passes to those of crystallization, thus.* "When a liquor "saturated with a salt is evaporated to a pellicle, "and sufficiently cooled, the salt forms in regular "crystals. Before being collected, the saline "particles floated in the liquor, equally distant "from each other; they acted therefore mutually "on each other, with a force which was equal at "equal distances, and unequal at unequal dis- "tances; so, in virtue of this force, they must "arrange themselves in a uniform manner, and "without this force they could only float in the "liquor without order, and unite therein very "irregularly."

It is only when this mutual action can produce sensible effects that the form of the molecule begins to contribute to the effects; then the mole-

* Opt. book III.

cule take an arrangement, according to which the affinity which constantly tends to unite them is exercised with the greatest advantage. In water, it is only at the degree which precedes congelation that an effect dependent on the figure which these moleculæ tend to assume can be perceived, and if the congelation is too sudden, their arrangement is not symmetrical; nevertheless, all the other effects of the force of cohesion do not experience any alteration.

The form which may be supposed in a malleable metal cannot be preserved, or entirely change its relations, when it is submitted to the action of the hammer, or drawn into wire; nevertheless, its properties remain absolutely the same, or experience only that change which is the natural result of the approximation of its particles.

The phenomena of crystallization are therefore a consequence of the weakness of the chemical action which produces it, and of the calm which secures it from disturbance; but it does not determine the combinations, or if, in some circumstances, it has a little influence, we must guard against attributing an extraneous one to it in the explanation of chemical phenomena, and especially against making the state of the combinations depend on it. If an action is given to the form of the moleculæ, how can the supposed different figures of five or six acids, mixed with water, and those of the elements of each acid, and of the water, be blended, so as that the whole

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shall, notwithstanding, form one homogeneous liquid, which will permit the transmission of the luminous rays?

If it was pretended, that the integrant moleculæ of sulphate of ammonia have a form, which not only determine its crystallization, but also its combination, they must derive this form from that of the moleculæ of the oxigen and the sulphur which formed the first combination, and afterwards from that of the hidrogen and the azote. But the sulphate of ammonia can form several sur-compositions which differ in their crystallizations: can elements so numerous, which must each contribute by its geometric properties to a particular figure, be subjected to regular and circumscribed results?

214. It seems to me, therefore, that we must separate the phenomena of crystallization which are owing to a weak and secondary action, in which even water can produce many modifications, although it only exercises a weak affinity on the integrant parts of crystals, (35); we must separate, I say, these phenomena from those arising from the affinity which produces combinations, and the force of cohesion which modifies their properties. (*Note XIV.*). They must only be considered as a consequence of the force of cohesion, which arises and is exercised so slowly, and with such moderation, that the form which the aggregates have taken can affect their union, but which does not enter into the forces which have produced

produced the combination ; it is only able to cause some modification in the force of cohesion. It cannot, therefore, be regarded as a cause of the combinations which are formed, and of the proportions which they receive. This is so true, that although the cohesion is made to disappear by solution, the properties of a salt which depend on its state of saturation are not altered, laying aside the inertia of the cohesion, the effects of which I have described.

If the combinations are seldom constant in their proportions ; if the form of the crystals is only an uncertain index of their state, we must not allow less latitude to the indications of the nomenclature, than observation obliges us to give to the proportions of the combinations themselves.

We cannot be certain of the constancy of the proportions in combinations, unless they are in a correspondent degree of saturation, which it is difficult to discover, except by the neutral state; in the combinations of acids and alkalis, and by the uniformity of the characteristic properties, such as those of water. The greatest number of combinations have only two degrees of saturation which can be considered as fixed, the term of the greatest, and that of the least saturation.

The names which express the composition of a substance must not receive a less extensive interpretation ; but when they are intended to designate the characteristic properties of a substance and

and its composition, a designation on which is founded the principal utility of nomenclature, it is important that a just idea should be formed of the acceptation which is given to it, and it is desirable that all chemists should agree to follow the same rules: with respect to expressions by which simple substances are indicated, or which are adopted for other purposes, they may vary with much less inconvenience. (*Note XV.*)

CHAP. II.

Of the Action of Solvents.

215. IN treating of solution, (*Chap. II. Sect. I.*), I considered only the effects which resulted from the mutual action of two substances which took a uniform state of liquidity or gazeity, according to the relative energy of each; I afterwards examined the separations of combinations which took place on account of their solubility. In these circumstances, the water, which I take here to represent the solvents, does not sensibly change the state of saturation of the substances which are in combination; the effects which it produces are limited to the modification of those

of

of the reciprocal action of the integrant particles of the combinations, so that it can only be considered as the opponent of solidity.

Nevertheless, the properties of a solution, whether of solid substances in liquids, (14), or of two liquids, (20), or, finally, of an elastic fluid in a liquid, (153), show, not only that it is the effect of a tendency to combination which produces a saturation of the properties, and which only differs in the intensity of that which forms saline combinations, but also that the laws of combination are manifested with the least disguise in the phenomena which it presents.

Since, therefore, a solvent only produces an effect inferior to that which unites the elements of a combination, we are confined to the consideration of the effects of the solubility which depend on it; but, in reality, it exercises a force similar to that of the affinity which produces combination, and whose effect is limited, in the solution of a solid, by the force of cohesion; in the solution of a liquid, by the difference of specific gravity; in the action of a liquid on a gas, by the elasticity; and in that of a gas on a liquid, by its volume and by the temperature.

The action of the solvents is not always limited to this effect on chemical combinations; but according to the reciprocal action of their elements, it may change the state of saturation, and then it must be reckoned among the forces which serve to produce combinations.

In

In this chapter I shall particularly occupy myself with the changes which may result in the state of combinations, especially in the proportions, of which I have pointed out the causes in the preceding chapter, from this action of the substances which are employed as solvents, and whose effect is most frequently neglected in the explanation of the results of chemical action.

I shall endeavour to distinguish the circumstances in which their action may pass unnoticed, and those in which it must be included among the causes of the phenomena whose explanation is given: for this purpose it is necessary to have recourse to properties which I have already examined under other relations.

216. The action of water on the acids and on the alkalis is generally so weak, compared with the force which produces their combination, that it should be entirely neglected, although in reality the mutual tendency to combination is weakened by all the force with which each elementary part is retained by a solvent, *minus*, that which it preserves to hold the combination in solution: thus, when an acid acts on an alkaline base, the action of the water does not commonly produce any sensible change in their mutual saturation; it only diminishes the energy of the acid opposed to the force of cohesion, because it diminishes its concentration in the ratio of its quantity; but when the liquid acts on a weak combination, and when the action which it exercises on each of the substances

which

which compose it is very different, the result depends on the relation of these forces; the liquid may then produce a change which occasions a difference in the combination, and alters the proportions of it. It is thus that water acts on sulphate of mercury; employed in a small quantity, it only dissolves it, but if it is more abundant, its action increases in proportion to its quantity, and it establishes new combinations, whose proportions depend on the state of the respective forces: in this case, the liquid cannot be considered as a simple solvent; its action is one of the forces which must be estimated in the change which is effected, and it becomes one of the elements of the combinations which are formed.

Many similar circumstances occur, in which the water does not simply produce a separation of the combinations, without changing their comparative saturation, but also occasions other proportions in the combinations which separate: we have seen, (202), that the acidulous phosphate of lime is brought to the state of neutral phosphate by the action of water: it produces this effect by successively determining two combinations, of which one is more acid, and the other has a greater proportion of base, until an insolubility and a state of combination arises, which at length resists all its action: when acidulous sulphate of pot-ash is decomposed by successive crystallizations, two combinations are formed by the action of water, at each crystallization, one of which is more

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more acid, and the other approaches more to the neutral state, and when at last this is attained, the reciprocal action of the elements has acquired an energy which does not permit the water to cause any further alteration in their proportions. If, therefore the action of the water does not produce any change in the state of the saturation of a combination, it can only be because it is inferior to what remains of the mutual tendency unsatisfied in the elements of the combination.

217. Thus, the chemical action of a solvent may be neglected with respect to the state of combinations, when other affinities, much more powerful, produce them; but it acquires importance in proportion as these affinities are weaker, and, finally, by its relative force it decides, in some circumstances, the compounds which are formed: the action of a liquid on a solid is not limited by the force of cohesion alone; but if the solid is a compound which has no great energy, it may establish two new combinations, the quantity and the proportions of the elements of which depend on the quantity of the water and the heat, and the concurrence of these agents diminishes the combination which remains in the solid state: by employing successive quantities of water, a series of combinations is produced between the two extremes.

Even when the water does not change the respective state of saturation, and when it appears simply to divide the combinations, its affinity in reality

reality contributes to the union of one base with one acid, and of the other base with the other acid ; it is it which determines the formation and separation of the most soluble combination, that is to say, that which opposes the least obstacle to it, and on which its action is the strongest ; but these effects are represented without inconvenience by the solubility of one combination, or by the force of cohesion of the other, as I have done when I considered the action of two acids on one base, or that of two acids on two bases, (*Sect. II.*)

Hence it results, that the only real distinction which is to be made relative to the action of water, is to consider if it produces any change in the state of the saturation, or if it effects separations, and determines combinations, whose saturation remains the same.

218. The observations which I have offered on the effects of water when it acts as a force opposed to cohesion, or as a principle of combination, are applicable to the other solvents ; but as their force and their other properties vary, different effects will result, whose importance must be appreciated : in this respect I shall consider only alcohol, of which, after water, the most use is made.

It must not be overlooked, that when I express the effects of the insolubility by the force of cohesion, I only mean by that, the relation to the solubility, in the solvent, which produces the phenomena, I use this expression to describe ; for the absolute

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absolute force of cohesion does not correspond exactly with the effect of the solvent. It is much better represented by fusibility, or by the effect produced by heat. For example, barites or lime, which totally resist heat, are nevertheless dissolved in a sufficient quantity of water. It follows, therefore, that the affinity of the water has been able to surmount great part of the absolute force of cohesion in these substances; but this first effect being produced by the affinity, it appears that it is only the solubility increased by the action of caloric, as it would have been without the presence of the solvent, which augments the proportions of the substance, naturally solid, in the solution; and that then the solution may be considered as the effect of a double solvent of the liquid and caloric, nearly as has been done by Lavoisier: * " Several different cases may be distinguished, according to the nature and habitudes of each salt. If, for example, a salt is but little soluble in water, and greatly so in caloric, it is clear that this salt will be very little soluble in cold water, and that, on the contrary, it will be very soluble in hot water; such is nitrate of pot-ash, and more especially oxygenated muriate of pot-ash. If another salt, on the contrary, is neither very soluble in water or by heat, it will be but little so either in cold water or in hot, and the difference will not be very consider-

* De la Solut. de Sels par le Calor. Trait Elém. tom. II.

" able:

" able: this is what takes place with sulphate of
" lime.

" It is obvious, therefore, that there is a necessary relation between these three things, the
" solubility of a salt in cold water; the solubility
" of the same salt in boiling water; and, the degree at which the same salt liquefies by caloric
" alone, and without the assistance of water; and
" that the solubility of a salt, in the heat or in
" the cold, is so much the greater as it is more
" soluble in caloric; or, which comes to the same,
" as it is susceptible of liquefaction at a lower
" degree of the thermometric scale."

Alcohol appears to preserve the same relations as water with a great number of substances, and particularly with the acids, alkalis, and saline combinations, and the principal difference which exists between these two solvents consists in the action of the alcohol being weaker, so that the force of cohesion opposes a resistance whose effect is greater: hence it arises, that the acids which have a considerable force of cohesion, such as the oxalic and sedative acids, do not dissolve in alcohol: it is the same with alkalis; those which have little solubility in water, such as lime, strontian, and barites, do not dissolve in alcohol; but those which are very soluble in water, such as pot-ash, and in general the deliquescent salts, can crystallize in alcohol, and sometimes with much more facility than in water.

The difference in the action of water and alcohol

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is not confined to these separations, which only arise from the greater effect of the force of cohesion opposed to the alcohol; changes of proportions, whose true cause may pass unobserved, and which have often led to false conclusions, may also result from this difference of action.

219. Sometimes different solvents are used, and in some cases successively, to effect by their means the separation of different substances: but the circumstances in which there is only a mixture of these substances, and those in which a combination exists must be distinguished.

It frequently happens in this latter circumstance, that the intervention of the solvent employed produces combinations which did not exist, while it is believed that only a simple separation is effected, and it is the weakness of its action which determines the combinations which are formed, because, with more energy, all the solution could have operated, and the combination would have preserved its integrity. Alcohol acts then on the combinations which are maintained by water as we have seen that water acted with respect to the acidulous sulphates and phosphates, by separating them into two combinations, which differ not only in their solubility, but also in their state of saturation.

220. Let there be an incrystallizable residue composed of pot-ash, nitric acid, muriatic acid, and lime, the mutual action of these substances, and that of the water which they retain, prevents the pot-ash from crystallizing

crystallizing with the two acids, or with that one which would be superior on account of its quantity, (58); let alcohol be mixed with this liquid, it will hold the combination of the lime with the acids, and that formed with the pot-ash will precipitate: it is not a simple separation of the nitrate or muriate of pot-ash, or of the nitrate or muriate of lime; for these substances would have produced a single combination in which each would exercise its own action. It is the alcohol which determines the formation and separation of these salts, because its disposition to unite with a salt with an earthy base concurs with the force of cohesion which belongs to the nitrate and muriate of pot-ash, and which opposes their solution in alcohol with more efficacy than their solution in water.

This separation is not complete; a small portion of the crystallizable salt is dissolved in the alcohol by the effect of the action of the salt with base of lime which renders it a little soluble in this solvent.

When in an uncrySTALLizable liquid there is an excess of acid or of alkali which is soluble by alcohol, the conditions of the liquid are changed by separating the excess, so that if a judgment is formed of the state in which it was, from the results obtained by means of this separation, it will be erroneous: thus, when the excess of pot-ash which opposed the crystallization of sulphate of pot-ash is carried off, a real combination with excess

excess of pot-ash is destroyed, and two combinations are formed which separate; one is the alcohol of pot-ash, and the other is the sulphate of pot-ash; but the first retains a small portion of the sulphate of pot-ash which is rendered soluble in the alcohol by the action of the pot-ash, and of which it cannot be deprived but by crystallization; and the second retains a small excess of pot-ash: even crystallization is not always sufficient to yield a uniform combination; for example, carbonate of pot-ash is obtained in a crystallized state by treating common pot-ash with alcohol, which dissolves the greatest part of the excess of the pot-ash; but the crystals retain enough to be deliquescent in the air.

I have just supposed an excess of alkali in carbonate of pot-ash; nevertheless, it is as accurate a combination as that of the neutral carbonate: but the alkali which is in excess with respect to the neutral state, and which produces a greater solubility, may be separated with more ease, because the chemical action is weakened by saturation. The action of alcohol, therefore, changes the combination which existed, and substitutes two new ones to it; the salt which crystallizes retains an excess of alkali, because the force of cohesion which causes the crystallization does not belong to determinate proportions, but begins to be energetic before arriving at its greatest intensity.

A similar effect is produced by means of other substances

substances which are equally capable of forming with pot-ash a more soluble combination than carbonate of pot-ash; thus Lowitz has shown, that carbonate of pot-ash could be obtained by a small quantity of acetic acid, the soluble combination with which permits the carbonate of pot-ash to crystallize, or, by the addition of a little sulphur, which forms also a very soluble hydrogenated sulphuret;* finally, oxygenated muriatic acid produces the same effect when it is not employed in a sufficient quantity to form the oxygenated muriate of pot-ash: if the solution of pot-ash, partly carbonated, is sufficiently concentrated, crystals of carbonate of pot-ash are formed at the commencement of the operation.

221. It is evident, therefore, that the solvents are to be considered under two relations, either as opposed to the force of cohesion, or as a constituent part of the combinations themselves; and, that the principles which have been advanced respecting chemical action must be applied to them under these two relations; but a solvent may be employed solely with a view to favour or moderate the action of an acid on a solid body, then its quantity may affect this action in a twofold manner, both because it is exercised on it by proportionally awakening its energy, and because it diminishes the concentration which it meets with within the sphere of activity.

* Journ. de Chim. par Van Mons. No. 3.

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Thus the solvents weaken the energy of the acids or of the alkalis, even when they cannot produce any sensible effect on their respective saturation; and if we then judge of the affinity of one substance by the effect it produces on another, we shall form a very false opinion. It may then be considered as inactive and as very inferior to that which is opposed to it, while by only diminishing the quantity of the solvent it will have a very different effect: thus pot-ash cannot attack sulphate of barites and phosphate of lime, if it is diluted with a certain quantity of water; but if it is boiled with these salts in a quantity of water only sufficient to dissolve the alkali, it decomposes them in part.

These effects of solvents, which depend on the difference of their energy against the force of cohesion were neglected when the order of elective affinities was established, to which alone the formation of combinations was then attributed: thus Bergman having dissolved phosphate of pot-ash in arsenic acid, and having added alcohol to the solution, which by dissolving the arsenic acid concurred with the force of cohesion of the phosphate of pot-ash, and by that means produced the separation of the latter, attributed this effect to a stronger elective affinity in pot-ash for phosphoric acid than for arsenic acid, and it is often by similar means that the elective affinities have been determined.

If alcohol is added to a sufficiently diluted solution

tion of lime in muriatic acid, with which sulphureous acid is mixed, sulphite of lime precipitates: for the same reason it might have been concluded, that sulphureous acid has more affinity for lime than muriatic acid; nevertheless when concentrated muriatic acid is poured on sulphite of lime, sulphureous acid is disengaged: the same principles would, therefore, have led to contradictory consequences. Besides, alcohol produces the same precipitates from a salt rendered soluble by an excess of its own acid; thus, from a solution of acidulous phosphate of lime, alcohol precipitates a less acidulous phosphate.

222. The considerations offered in this chapter show that the solvents really exercise a chemical action, differing only in the intensity from that which produces the most powerful combinations; but as it varies in this respect, and especially in its relation with the forces which produce other combinations, there are cases in which it may be neglected, because it occasions no sensible alteration in the saturation, and there are others in which it intervenes as a principle of combination.

When it does not change the state of the saturation, its effect is limited to the solubility of the combinations; and it must only be considered as a force opposed to solidity: it weakens the action of the other substances opposed to the solidity, in the ratio of its quantity which exceeds that necessary to produce liquidity, by diminishing the quantity of these substances which can act, and

by employing part of their energy: it divides a single combination into two combinations, of which one is more soluble, and the other separates by the force of cohesion which it is enabled to oppose to it.

Solvents frequently exercise both actions, and contribute by one to the separations which take place, and by the other to the proportions of the elements which are established.

From the difference of intensity in the action of two solvents, such as water and alcohol, considerable differences may be produced in the combinations which separate: a stronger action prevents the crystallization which would have taken place in a weaker solvent, and for the same reason the latter can produce separations, and proportions of combinations, which would have remained blended in the liquid state with a solvent of greater energy.

This exhibits a striking example of the influence which words have on the ideas we form, and even on the results of observation. We begin by considering a solvent as an agent which only disposes other substances to form combinations, because, in reality, it does not produce any other sensible effect, when it is not the cause of the separation; and we consequently neglect its action in other circumstances, because, in them, it retains the name of a solvent.

It is difficult to attain a precision of language which can prevent all confusion; but it must never

never be lost sight of that all the substances which are present exercise an action; and that, if there are circumstances in which it may be neglected, there may be others in which it contributes efficaciously to the result.

CHAP. III.

Of Efflorescence.

223. SOME saline substances, and particularly carbonate of soda, have the property of separating, in a certain degree of humidity, from the substances with which they are combined. Scheele was the first who perceived that this property might produce changes in the combinations.*

This force, by which the moleculæ unite in suitable proportions, to form an invariable combination, and separate from the other substances which have an action on them, is very analogous to that which produces crystallization in a liquid; although from the difference of circumstances the effect is of a contrary description: it appears, that in these circumstances a combination which would be quickly destroyed, if its action was in competition with that of the substances contained in a

* Mém. de Chim. tom II.

liquid,

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liquid, is continually separating at the surface by very small portions; by this means its molecules are successively withdrawn, and their reciprocal action then brings them into masses, as in crystallization: but whatever may be the difference which exists between this effect and that of the common crystallizations, I shall endeavour to point out its consequences, in the phenomena to which it contributes, by designating it under the name of efflorescence, and by considering it principally as a property only belonging to some substances.

224. If muriate of soda is in conjunction with lime, in a suitable degree of humidity, the action of the soda on the muriatic acid is weakened by it: it partakes of that of the lime on the carbonic acid of the atmosphere; but, from being diminished by saturation, it would soon be inefficient against the force of cohesion of the carbonate of lime if a separation was not produced by efflorescence: the decomposition of the muriate of soda, therefore, continues until a sufficient quantity of muriate of lime is formed, because the muriatic acid, being necessarily divided between the two bases in the ratio of their action, a period arrives at which their forces are balanced.

The small quantity of carbonic acid which is combined at first in the whole mass does not produce a force of cohesion which can overcome the opposed forces, (77); it is only sufficient to determine the successive efflorescence: but if the quantity

quantity of carbonate which is separated is suddenly dissolved, then the force of cohesion has sufficient intensity to precipitate the carbonate of lime, and contrary combinations are obtained by this sole condition of the quantities.

Efflorescence also produces a separation of carbonate of soda, whenever this is in contact with carbonate of lime in a suitable degree of humidity; then, by means of the action exercised on it by the muriate of soda, but little solution of carbonate of lime is made; but the combination of carbonic acid with the soda, and the simultaneous separation are decided by the disposition to efflorescence, and the phenomenon continues. The circumstances which favour efflorescence are, a suitable mixture of muriate of soda and carbonate of lime, and, a humidity maintained at an elevated temperature; the vicinity of a porous body also favours the decomposition of muriate of soda, by facilitating the efflorescence and separation of carbonate of soda; but, although there is but little difference between the conditions of this decomposition and that obtained by lime, it appears that the first requires a much greater interval of time, and perhaps some more favourable circumstances, such as a more elevated temperature; hence it probably arose that Scheele did not obtain this decomposition by using carbonate of lime.

225. These circumstances, which I have observed on the borders of the lake Natron, appear to

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to me sufficient to explain the continual formation of the immense quantity of carbonate of soda,* and it is probable that the production of carbonate of soda noticed in other deserts, as well as on the surface of some vaults and walls, is owing to similar circumstances, or to such as are but little different.

It is also to a similar cause that the decomposition of muriate of soda by plates of iron kept in a damp place must be attributed: the carbonate of soda effloresces on their surface, and is decomposed by being immersed in the drops of muriate of iron which form at the same time.

Scheele, to whom the principal observations on this subject are owing, proved that decompositions also took place with sulphate and nitrate of soda, but not with the same salts with base of pot-ash, and he very properly attributed this difference to the efflorescent property of the carbonate of soda.

It is probably for the same reason, that several plants on the borders of the sea can decompose muriate of soda in favourable circumstances, that is to say, when they do not grow in the water; for then they only contain muriate of soda which is not subject to decomposition; the carbonate is only formed when they grow on the shores, in a soil impregnated with muriate of soda, and which has no more humidity than is required for the ef-

* Mém. sur l'Egypte.

fluorescence;

florescence; but this decomposition does not take place in plants which only contain salts with base of pot-ash.

226. Although efflorescence is a property which is more energetic in carbonate of soda than in other salts, several of them are not destitute of it: it appears to me that it is from this cause that in old rubbish, impregnated with salt-petre, the nitrate of pot-ash separates from the salts with an earthy base, and is principally found in the most elevated parts, while those which are contiguous to the soil contain principally a salt with a calcareous base.

The formation of sulphate of alumine which takes place in the surface of granites and porphyries which have been long kept wetted with sulphuric acid, as was done by Bayen;* and which he employed advantageously in the analysis of these stones, appears to me to be owing to the same cause.

Finally, from the efflorescent property possessed by the acidulous sulphate of pot-ash, arborisations rise, and are formed above a combination which retains a greater excess of acid than is suitable to the constitution of this salt; which shows, that in this phenomenon, while one new combination tends to separate by efflorescence, another tends to retain the excess of the element which opposes this effect.

* Journ. de Phys. 1779.

Although

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Although efflorescence produces but a small number of effects, it must not be neglected, since it serves to explain the production of some combinations which are opposed to those formed in ordinary circumstances, and which may be applied with utility in the arts.

We find in this a striking instance of combinations produced by a slight circumstance, and in an inverse order to that which is attributed to the elective affinities.

CHAP. IV.

Of the Propagation of Chemical Action.

227. CHEMICAL action is exercised with more or less rapidity, and this circumstance frequently has great influence on the results: the action of caloric offers some relations with this property of other substances which it is useful to examine.

Combinations, which appear constant in their proportions, are destroyed by a slower action than that which produced them; other proportions are established, and give place in their turn to new combinations: hence the conclusions drawn from observation vary according to the instant at which it is made: that is taken for the last result of chemical

mical action which precedes other changes which are neglected, and a state which is only transitory, is attributed to the election of affinity.

Sometimes, therefore, chemical action appears to be instantaneous, sometimes its effects are very slow, and a considerable space of time is necessary to enable the forces which are present to attain a state of equilibrium. What are the dispositions in substances which produce this difference? What are the circumstances which favour or lessen this effect?

228. It must be observed, in the first place, that, independently of every other circumstance, chemical action is much slower when it is weak than when it is brisk; and as the action of a substance is weakened in proportion as its saturation advances, it is only the latter stages of this saturation which require a much longer interval of time to be completed than is necessary for advancing it to that period: thus, in mechanical operations, a strong impulse causes a body to pass through the same space in a much shorter time than a weaker impulse.

It is therefore in weak combinations that this resistance to saturation is more especially observed; such are the solutions of salts in water, compared with the action of acids with alkalis, and a great difference is also observable between the beginning and the end of a solution: water cannot be brought to that point of saturation which

which its action and the resistance it has to overcome will admit of, without some trouble.

The combination of an acid with an alkali which is effected by a much stronger force than that which produces the solution of a salt by water, is also much quicker, until it approaches the state of saturation; then its progress becomes slow, and a period arrives at which the papers used as tests frequently announce at the same time both acidity and alkalinity, and it is not until after a considerable space of time that it can be ascertained which of the two really predominates.

Agitation greatly accelerates the completion of a solution, or of a combination: its effect depends wholly on the difference which there is between the action of a substance when it is far from a state of saturation, and when it is near to it: by it a strong and brisk action is substituted for a weak and slow one.

When water acts on a salt to dissolve it, that part which is contiguous to the salt is at first in a more advanced stage of saturation than that which is immediately above it, and so on in succession to the surface; there is therefore only a slight difference of saturation between each stratum, and, with respect to each other, they are in that state of saturation in which the action is weaker and slower, and the difference in the specific gravity can also have a marked influence on the effect of a weak tendency to combination; but if the

most

most saturated parts of a liquid are brought into contact with those which are the farthest from saturation, a much brisker action is established, and the effects are accelerated; agitation therefore is useful in rendering the solution uniform much more quickly, and this may be applied even to the strongest combinations, when the action of the substances which form them, approaches the term of saturation.

This effect may be obtained from the specific gravity established between the strata of a liquid, by the solution of a salt itself, if the solution is effected at the surface of the liquid, so that this circumstance alone produces solution much more quickly: then, as the water dissolves the saline moleculæ, it descends on account of the specific gravity it has acquired, and that part of the liquid which was at the bottom rises to the surface by its specific lightness. By this means a circulation is established which is easily rendered visible, by plunging a tube filled with sulphuric acid into a saucer filled with water; this current, which is pretty rapid, carries with it the small insoluble bodies which may have been added to the liquid.

It appears to me that Citizen Beaumé was the first who paid attention to the circulation occasioned by the change of the specific gravity when a salt is dissolved at the surface of the water, and who at the same time made a useful application of it to the solution of the saline residues which are found at the bottom of a vessel: in fact, if the

neck

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neck of a vessel containing a salt hardened into a mass is plunged into water at its surface, we shall see the water which has effected a solution descend in a current, and the pure water, or that which is less saturated forms a contrary current by rising to replace it; whence it follows, that the solution of a salt is effected much more rapidly by the continual renovation of water whose action is less weakened by saturation, than if a quantity of water whose different strata would have but little difference of saturation was kept upon this salt. Some time past Welter applied this property to all solid substances which dissolve more quickly when they are retained at the upper part of the solvent, and, from him, I have given an example in the solution of the common pot-ash, intended for the leys in the operation of bleaching, by oxygenated muriatic acid;* while, from the contrary action, the solution of gazeous substances must be made at the bottom of the liquid. These considerations have become familiar to chemists.

229. It is probable that, independent of the slowness of action arising from the weakness of the affinity, substances are distinguished by a property that may be compared to the conducting property of heat which I am about to examine, so that in some the action has a peculiar slowness which is independent of its energy: thus, although, at first, sulphuric acid exercises a brisk

* Journ. des Manufactures et des Arts.

action

action on water; although it retains it strongly, it nevertheless is difficult to bring it to a uniform solution, so that when the liquor is interposed between the eye and the light, it shall not appear striated: it is the same with alcohol; while muriatic acid and acetic acid acquire a uniformity of solution much more rapidly.

The hygrometric effects, as well as the solution of a salt, are owing to the tendency of a substance to combine with the water which is held in solution by the air. In the same manner the action of hygrometric substances is observed to relax as they approach the extreme term, and some of these substances pass through the different degrees with much more rapidity than others; thus hair has a much quicker effect than whalebone: this difference does not depend on the weakness of the hygrometric power, for lime, which exercises it with at least as much energy as muriate of lime, nevertheless produces its effect much slower; it must therefore be owing to a greater or less faculty of propagation which distinguishes these substances, and which is independent of the energy of the affinity.

The slowness of the action of elastic fluids is very great, when the force which tends to produce the combination is feeble: thus oxygen gas dissolves carbonic acid but slowly; it is only in a considerable space of time that its action on iron is exhausted; although the alkaline sulphurets exercise a pretty brisk action on oxygen, they never-

nevertheless absorb it very slowly; the air acquires the extreme degree of humidity with difficulty, and notwithstanding the vapour of water, in a vacuum, quickly acquires the degree of tension communicated by the temperature: on the contrary, some odorous substances dissolve and spread themselves rapidly through an extensive space of the atmosphere.

The action of elastic fluids is also accelerated by agitation which brings the least saturated parts together, and it is probable that the differences of specific gravity may occasion currents which hasten the equilibrium of saturation, as in liquids; but these effects will also differ according to the position of the substance which dissolves or enters into combination, and they will be complicated with those of the temperature.

230. The faculty of combining more quickly with one substance than with another sometimes produces precipitations, which may be considered as accidental, and which do not take place if the circumstances render the action slower. Bergman observed that when concentrated sulphuric acid was poured into saturated solutions of sulphate of pot-ash, alum, sulphate of iron, corrosive mercurial muriate, or other salts which water dissolves with difficulty, that the salts were rapidly precipitated; but if the sulphuric acid was poured in by small portions and the liquid agitated, these precipitations did not take place. The same phenomenon is observed on suddenly mixing an aqueous

aqueous solution of muriate of barites with concentrated muriatic acid, and in a great number of other circumstances, in which it is seen that a precipitate is formed at the first instant of the mixture, and afterwards re-dissolved slowly, or more quickly by the assistance of heat or of agitation.

If affinity requires a greater or less length of time to produce combinations, this effect is not less marked in the reciprocal action of the moleculæ, by which they adhere and form crystallizations: but if motion accelerates the formation of crystals by bringing the moleculæ into the most favourable positions, it must also be so moderate as only to determine the first formation of the crystals, which, that the crystallization may be regular, must afterwards be completed in undisturbed tranquillity.

It appears that the action by which the moleculæ of a solid mutually adhere, is continued long after the moment at which they enter into contact; for it is frequently observed that a precipitate recently formed in a liquid, gradually acquires a considerable hardness, without its being possible to attribute it to any other cause, and that different bodies harden by age, even after their evaporation has ceased.

231. With respect to the communication of heat, bodies possess a property analogous to that which I have just noticed: while the difference of temperature between two bodies is great, the com-

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mical action which precedes other changes which are neglected, and a state which is only transitory, is attributed to the election of affinity.

Sometimes, therefore, chemical action appears to be instantaneous, sometimes its effects are very slow, and a considerable space of time is necessary to enable the forces which are present to attain a state of equilibrium. What are the dispositions in substances which produce this difference? What are the circumstances which favour or lessen this effect?

228. It must be observed, in the first place, that, independently of every other circumstance, chemical action is much slower when it is weak than when it is brisk; and as the action of a substance is weakened in proportion as its saturation advances, it is only the latter stages of this saturation which require a much longer interval of time to be completed than is necessary for advancing it to that period: thus, in mechanical operations, a strong impulse causes a body to pass through the same space in a much shorter time than a weaker impulse.

It is therefore in weak combinations that this resistance to saturation is more especially observed; such are the solutions of salts in water, compared with the action of acids with alkalis; and a great difference is also observable between the beginning and the end of a solution: water cannot be brought to that point of saturation which

the point at which the heat is communicated, and brings that part to it which is least dilated : but these effects, which are owing to the same cause, follow an opposite motion, because the specific gravity diminishes in one case and augments in another, so that the observations I have made on the solution of a salt which is effected at the surface, (228), must be applied to heat which is communicated at the lower part of a liquid.

It follows from this, that a great difference is observable in the communication of heat according as it is made by the lower or upper part of a liquid ; the latter must be much slower, since there is a constant effort in the moleculeæ to remain in separate strata which have only a gradual and slight difference of temperature, while in the first the difference of the specific gravity tends continually to bring the parts least heated to the centre from which the heat emanates.

Another cause also increases this effect : while the heat penetrates with difficulty from the superior strata to the inferior, vapours are formed at the surface which being afterwards chilled by the bodies they encounter, give place to those which succeed them, so that the liquid gradually loses its temperature by the sides of the vessel which contains it, and especially by the surface ; by this means the communication of the heat to the different strata becomes slower and more difficult.

These different effects must be carefully distinguished

guished in the consideration of the phenomena offered by the communication of heat between bodies which are in different states.

The resistance opposed by the difference in the conducting faculty, sometimes produces a distribution of heat, either in liquids or in solids, in which one substance appears to take nearly the whole, while another experiences but little change in its temperature: thus, when a bad conducting substance is associated with other bodies, the heat, which might be slowly communicated to this substance, and bring it to a uniformity of temperature, if it was surrounded with an atmosphere from which it could receive heat gradually, passes much more rapidly into the other bodies, while it is communicated by a bad conducting layer to the next; it is therefore quickly weakened, and as the effect is increased as the temperature lowers, this substance scarcely acquires a sensible heat at a small distance from the centre of emanation of the caloric.

232. The propagation of chemical action has also a peculiar character in compound substances, according as they act by a resulting affinity, or by their elementary affinities.

If a substance acts by a resulting affinity, it produces its effect more or less quickly, which does not sensibly relax, unless when its action is much weakened; it comports itself like the simple substances: but if it acts by its elementary affinities, unless its action is very brisk, it acquires a dullness

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a dullness much greater than that which arises from the weakness of its action : thus, when nitric acid is mixed with an alkaline base, it quickly succeeds in bringing it to the state of neutralization, even when the acidity and alkalinity are very much weakened by a great quantity of water ; but when nitric acid and muriatic acid are mixed, although a sufficient agitation is employed, the oxygen separates slowly from the azote to combine with the muriatic acid, and to exhale with it in oxygenated muriatic acid ; on the other hand, the nitric acid insensibly dissolves the nitrous gas, and remains combined with another portion of the muriatic acid, in the state of nitro-muriatic acid. It is not until the expiration of a long space of time that the forces which act arrive at a state of equilibrium.

Hence it frequently happens, that a substance begins to act by a resulting affinity, and afterwards acts slowly by its elementary affinities thus a metallic solution in nitric acid often changes its nature when it is kept ; it loses the state of saturation which it had at first, the metal becomes more and more oxidized, and sometimes a greater or less quantity of ammonia is formed, although the temperature and other circumstances have not been favourable to this change.

The more the elementary affinities lose their force by the new combinations which produce a higher degree of saturation, the more is their immediate action diminished, (184) ; the more dullness

ness it assumes. When oxygenated muriatic acid is poured into a solution of iron a little oxidized, the metal very soon becomes completely oxidized, because the resulting affinity of the oxygenated muriatic acid is very feeble, and consequently offers but little obstacle to the action of the iron: if a solution of oxygenated muriate of pot-ash is made use of, in which the oxygen is in a greater proportion, but retained by a stronger resulting affinity, the same effect is not manifested until after a much greater space of time, and it is continued longer. The action of caloric, which diminishes the resulting force, accelerates also that of the elementary affinities, so that, in the preceding experiment, a very rapid effect may be obtained by means of it.

When iron decomposes nitric acid, and disengages nitrous gas from it, its action is sometimes very slow at the commencement; so, if the acid is too little concentrated, or the temperature too low, it takes place with difficulty; afterwards the action becomes brisk and tumultuous, although the state of the proportions becomes more and more unfavourable: the heat disengaged diminishes, proportionally, the effect of the resulting affinity, it acts also on the iron by diminishing its force of cohesion; but, in this case, that effect is very small in comparison with the other.

This inactivity of the resulting affinity is observed in the mixtures of metallic solutions, in which the metals are at different terms of oxidation;

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tion; it is not until after a greater or less length of time that they attain a uniformity of oxidation, and that they take the proportions of acid required by their state, either to remain in the liquid state, or to form precipitates: but as my opinion with respect to these last phenomena differs from that which is generally received, I shall postpone the discussion to another part of this work.

283. The considerations I have offered in this chapter show the importance, in estimating the effects of chemical action, of directing the attention to its propagation, and to those circumstances which can modify it; and how we may be deceived by considering, as the limits of the affinity of a substance, those combinations which it may produce at the commencement of its action.

When chemical action is weak, its propagation is slow, so that we are easily led into an error, by too much haste to obtain a result; thus many combinations, which were believed to be impossible, have been realized, by employing the requisite time: I shall select two from the great number which offer themselves.

Hidrogen gas is considered as a substance which is protected by its elasticity from the action of oxygenated muriatic acid, nevertheless Cruikshank found that by leaving hidrogen gas in contact with oxygenated muriatic gas for twenty-four hours, a complete decomposition of the oxygenated muriatic acid took place, which returned to the

the state of muriatic acid while the hidrogen formed water: the slow decomposition of carbureted hidrogen gas also takes place with oxigenated muriatic acid gas, and the result is water and carbonic acid.* It is by means of a very slow action that, in germination, the hidrogen gas is converted into oxi-carbureted gas, according to the observations of Sennebier and his interesting co-operator Huber†; it also appears to have been discovered by them, that when a mixture of oxi-carbureted gas and oxigen gas is left for a length of time over water, carbonic acid is gradually formed.

The slowness of the propagation of chemical action is diminished by the methods which bring together the parts whose state of saturation is the most distant: it is thus that agitation forwards the equilibrium of saturation in liquids and elastic fluids.

The difference of specific gravity which tends to retain the least saturated strata of a liquid at a distance from the salt when the water is placed above it, produces a different effect when the solution takes place at the surface; then a current is established which brings the least saturated liquid to the surface of the salt in solution, and the effect of this circulation is the same as that of agitation; it brings the parts whose saturation is the most

* Bibl. Britan. tom XVIII,

† Mém. sur la Germination.

different

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different into contact, and accelerates the reciprocal action.

Independently of the energy of their action substances seem to have a different disposition to produce the combinations which they form with more or less rapidity: they are better or worse conductors of chemical action, and when this property varies to a certain extent, it may at the first occasion combinations to which, by a slower action, others are substituted, until the equilibrium of affinity is established.

In respect of heat, bodies have a property analogous to the preceding; they are better or worse conductors: the propagation of heat is therefore much more rapid when there is a great difference in the temperatures, so that, in liquids or elastic fluids, agitation, or the circulation which is established on account of the difference of the specific gravities, produces the same effects as are observed in the solution of a salt: in the explanation of the phenomena arising from the communication of heat in liquids and elastic fluids, we must therefore include their conducting property, the distance of the temperatures, and the effects of the specific gravity which alters the position of their moleculæ. (*Note XVI.*). Heat intervenes in solutions, and by the movements it occasions by changing the specific gravities, and by the diminution it produces in the resistance of the cohesion, it establishes a greater difference between the opposing forces.

The

The analogy which I have pointed out between the combinations of caloric, and the other chemical combinations, is here extended to that observed between the propagation of chemical action which produces solutions, and that of heat which tends to produce an equilibrium in bodies of different temperatures.

In compound substances, particularly in those containing elements, naturally gaseous, the resulting affinity is much quicker in its action than the elementary affinities, even when the opposing forces are capable of destroying it, unless they have a great preponderance; whence it is frequently observed that a combination formed by a resulting affinity, gradually yields to the action of the elementary affinities.

SECTION VI.

Of the Action of the Atmosphere.

CHAP. I.

Of the Constitution of the Atmosphere.

234. THE atmosphere intervenes in a great number of chemical phenomena, by the dissolving action it exercises on liquids and elastic fluids, by the obstacle which it opposes to their natural dispositions, or by the combination of one of its elements.

It must therefore be considered under these relations, with a view to discover the part it takes in these phenomena; but its constitution varies its action.

The constitution of the atmosphere is the result of the conditions in which it is found; that is to say, of the pressure it experiences, of its temperature, and of its humidity. I have already examined the

the comparative effects of pressure and temperature on the gases in general (109); but they require a more particular application with respect to the action of the atmosphere, and to the dispositions of the liquids which it tends to dissolve.

Experiment has shown that the volume of the atmosphere diminishes in the ratio of the weights which compress it: all the permanent gases follow the same law; but a distinction must be made with respect to the elastic vapour of water which it holds in solution, according to the proportion found in it: if the air is saturated with it, the elastic vapour cannot undergo a diminution of the space it occupies, without a part, proportionate to the diminution, resuming the liquid state (167); but if the space is increased, it dilates like the other gases and then the hygrometer moves towards dry: when the air is not in a state of saturation, it approaches that term in proportion as it is compressed, and the hygrometer moves towards humidity; but when it has arrived at the term of saturation, it can not be farther contracted without part of the aqueous vapour separating in water; all which remains in solution retains the same degree of tension: thus compression reduces the volume of elastic vapours as it does that of the permanent gases, as far as the term of saturation; it then reduces the quantity.

235. We have seen (108) the law which the dilatation of gases by heat is subject to: but the elevation of temperature produces effects on the elastic

elastic vapour, or rather on the liquid tending to form that vapour, which deserve a particular consideration.

1st. It dilates the elastic vapour like a gas and augments its tension, so that the vapour makes an equilibrium with a column of mercury, which is in the same relation as the tensions, to that which produced the first tension: the vapour of water which at 15 degrees could raise the mercury six lines, will raise it nearly nine at a temperature of 80° or will be compressed by this column to preserve its first volume.

2d. It augments the quantity which occupies a determinate space, or which is dissolved in a volume of air, so that if there is not water enough to satisfy this condition the heated air is consequently removed from the degree of saturation, and causes the hygrometer to move towards dry.

But if there is water enough to produce saturation, the tension increases in a much greater proportion than in the preceding supposition, so that a much more considerable effect is added to the first.

The quantities of water which dissolve in a volume of air, by the elevations of temperature, are therefore in a much greater proportion than the dilatations: according to the observation of Saussure, the cubic foot of air saturated with water contains nearly 11 gr. at 15° of the thermometer; and at 6.78° it can only contain five grains.

Hence

Hence it will be seen why air which is cooled by dilatation, deposits water: the cold produced by the dilatation has a much greater effect on the quantity of water held in solution, than the augmentation of the space which it occupies: this explains why, in a machine used in the Hungarian mines*, the air which is compressed by the weight of a column of 200 feet of water deposits snow and small icicles when, by the opening of a cock, it is permitted to resume the state it would have had at an ordinary pressure.

236. Since the effort of the elasticity is the same when water, by its tension, raises a column of mercury in a vacuum, or when it has already taken the elastic state (165), we may ascertain, by the effect which it produces in one circumstance, that which might be obtained from it in another, and, by the tension of a liquid, we may estimate the elastic force of the vapour at different temperatures.

Betancourt has made some very interesting experiments on this subject †; but although they have a sufficient degree of accuracy for the end he proposed, they have not enough, particularly in the inferior degrees, to ascertain the laws of dilatation: thus he obtained no effect in the first four degrees of the thermometer, and he had but 0.14

* Philos. Trans. vol. lii.

† Essai experimental et analytique, etc. Prony. Journ. Polytechnique, Cahier I.

inches for 10° while the observation of Van Martum gives 0.40 inches.

Volta, in his researches, has distinguished as I have done since, the effect arising from the increase of tension by the elevation of temperature, and which follows the common law of all the gases, from that which is produced by the formation of a new vapour, which, itself, takes the tension given by the temperature, so that he was enabled to account for the two causes which produce the increase of the elastic action of a liquid, or of the vapour which it forms by heat : he observed that in these effects, all the liquids follow the same law, not only when they have arrived at the term of ebullition, but at terms equally distant from that of ebullition : he remarked that the elastic effort was nearly doubled from 15° to 13° of Reaumur's thermometer.

I do not offer these results, which I have collected from his conversation, without doubts, they are incomplete, and he purposes to give them greater precision.

237. Dalton has just published an important Memoir on the same subject: I shall give a summary of it, such as it is found in the *Bibliotheca Britannica*.* I shall apply the principles which I have endeavoured to establish to it, and I shall discuss the physical hypothesis which he uses to explain his results.

* Bibl. Brit. tom. xx. and xxi.

" The author takes a barometer tube perfectly dry, he fills it with mercury previously boiled, and he marks that part of the tube at which the mercury remains suspended, forming a Torricellian barometer. He graduates this tube in inches and tenths, by scratching it with a file; he then, after having taken out the mercury, wets it with water, or any other liquid whose vapour he means to examine; he fills it again with mercury, carefully excluding the air, and when the tube has been adjusted for some time, the liquid with which its inside had been wetted collects gradually above the column of the mercury, where it forms a small stratum.

" To give the vapour, which then forms in the Torricellian vacuum, that temperature which he wishes, the author fixes this barometric tube through a cork, in a glass tube two inches in diameter and 14 inches long. The barometer is retained in the axis of this tube by two corks which it passes through, in the upper one of which there is a second opening for the purpose of filling the large tube with water more or less heated, as far as the temperature of 155° ($54\frac{1}{2}$ R.)

" For higher temperatures, the author employs a siphon barometer, the long tube of which he incloses in a tube of tin, which can support boiling water, and he judges of the descent of the mercury in the invisible part of the tube, by its ascent in the inferior branch. This method supposes that the tube is of equal diameter through its whole length.

" By an air-pump, furnished with a barometer gage, the force of the aqueous vapour at different temperatures above that of boiling water, may be also determined. A phial half filled with warm water, into which a thermometer is immersed, is placed under the receiver; the vacuum is gradually formed, and at the instant at which the water begins to boil from the pressure of the air being diminished, the degree of the thermometer and that of the gage are marked. The height of the mercury in the latter is the exact measure of the force of the vapour: this method is applicable to other liquids.

" By employing these different processes, and by repeated experiments, the results of which he compared with great care, the author has arranged a table of the expansive forces of aqueous vapour for each degree of Fahrenheit's thermometer, from the freezing to the boiling point; and the examination of the results having shown that they followed a law sufficiently regular, and which is nearly correspondent with a geometrical progression, the ratio of which decreased but little, he was induced to extend his table, on the one side as far as the freezing point of mercury, and on the other to 325° Fahr. (150 $\frac{1}{3}$ Reaum.) (The publishers have given this table.)

" It is known that there are liquids more evaporable than water, such as ammonia, ether, alcohol, &c. there are others which are less so, such as mercury, sulphuric acid, muriate of lime, solution

tion of pot-ash, &c. and it appears, according to this author, that the force of the vapour of each of these liquids, in a vacuum, is proportionate to its evaporability. M. de Betancourt maintained that the force of the vapour of water and that of spirit of wine are in constant proportion, that is to say, nearly as 3 to 7. The results of the author's first experiments were nearly the same, but as he proceeded they were more different, and after much labour on six different liquids, he arrived at this general conclusion, to wit, "that reckoning from a certain vapour of a given force, the variation of this force, by the changes of temperature, is the same in all liquids." Thus taking as a common term the force which sustains thirty English inches of mercury, that is to say, that of *every liquid in a state of ebullition in the open air*, it will be found that *aqueous* vapour loses *half its force* by a diminution of 30° F. in its temperature: it is the same with *every other liquid*; its vapour loses *half its force* by being cooled 30° below its own peculiar term of ebullition, and the same force is *doubled* in the *vapour of every liquid*, as in that of water, by an increase of 40° F. above the boiling point of the liquid in question.

"The author commences the series of experiments which led to the above conclusions with sulphuric ether; this liquid entered into ebullition at 102° F. ($31\frac{1}{2}$ R.) He introduced a small quantity into a barometer tube and found that its vapour, at a temperature of 62° F. ($13\frac{1}{2}$ R.) sus-

tained 12.75 inches of mercury. This is the force of aqueous vapour, at 172° ; now these two temperatures are 40° F. distant from the boiling points of water and ether, to wit, from 102° and 212° . The author proves the same correspondence in the other parts of the scale below the term of ebullition: he also proved it at the temperatures above the same term by means of a siphon tube, into whose short branch he introduced some drops of ether, the vapour of which raised a more or less considerable column of mercury in the long branch, in the ratio of the temperature communicated to the ether, by plunging the short branch into hot water. He found that at 147° the vapour of ether had a force equivalent to 64.75 inches of mercury. This is also the force of the vapour of water at 257° which is 45° from the boiling point of water as the other is 45° from that of ether.

" By a skilful disposition of the apparatus, the author was enabled to submit the vapour of ether to the temperature of boiling water: its force then was equivalent to 137.67 inches of mercury. This temperature (212°) is 110° above that of boiling ether. Now, water at 322° that is to say, 110° above its boiling point raises 137.28 inches of mercury: the law in question is therefore proved at every degree of temperature examined.

" In the experiments on the vapour of spirits of

of wine, the author found that the force of this vapour exceeded that of the aqueous vapour a little, at the same distance from ebullition. He attributes this difference to the difficulty of preserving the alcohol at the same degree of rectification during the experiment; besides the difference scarcely exceeded two inches, a quantity within the limits of inevitable errors in this kind of experiments. The same difficulty as those he met with in the experiments on spirit of wine, was attended with greater inconvenience in those with ammonia.

" Muriate of lime, which entered into ebullition at 290° , that is to say, at 18° above the temperature at which water boils, introduced into a Torricellian vacuum, and heated successively to 55° 65° 70° and 95° Fahr. produced depressions of the mercurial column, which agreed very well with those produced by the aqueous vapour at the same distances from the boiling point of pure water."

The results which I have detailed and which point out the regular movement of all liquids and of all elastic fluids, in the progress of the elasticity which they receive from caloric, show that the reciprocal action of the moleculæ either produces no effect, or becomes uniform from the term at which the influence of the force of cohesion ceases: it is then modified by the action of caloric alone, which by combining to an equal degree of saturation, produces effects which are similar, when they are disentangled from those of the causes which act in a contrary manner.

238. Dalton has examined another series of phenomena: he determined the dilatations experienced by the air, when in contact with a liquid, according to the elastic tension of the liquid.

" In this course of experiments, he employed manometers composed of straight cylindrical tubes, hermetically sealed at one of their extremities, and $\frac{1}{4}$ of an inch in their internal diameter. They were divided into equal parts; a drop or two of the liquid to be submitted to experiment was put into the bottom of the tube, and after drying it well within, common air or some similar gas was admitted, and kept in by a column of mercury, from $\frac{1}{10}$ to 30 inches long, according to circumstances. The sealed extremity of the manometer was then plunged into water at a given temperature, and the expansion of the elastic fluid occasioned by this temperature was indicated by the motion of the mercury.

" The dilatation of dry air had been previously ascertained, and here the author notices, that according to the experiments which will be the subject of a subsequent essay, the expansibility of all the elastic fluids is the same, or nearly so, in similar circumstances. A thousand parts of any one of these fluids fills a volume from 1370 to 1380 parts by a heat equivalent to 180° F. (80 R.) and this dilatation takes place in a progression nearly uniform.

" The following is the simple formula of combined dilatation, when a vapour is mixed with a gas

gas, resulting from all the experiments he made between the temperatures of ice and boiling water.

" Let i , be the space occupied by a dry gas at a given temperature; p , the pressure which it experiences, expressed in inches of mercury; f , the elastic force of the vapour of the liquid, at the same temperature and in a vacuum: at the moment of the mixture a dilatation takes place, and the space occupied by the two fluids soon becomes

$$= \frac{p}{p-f}$$

" Thus, for example, when aqueous vapour is mixed with air, there is $p=30$ inches; $f=15$ inches, at the given temperature, (180° F.) then

$\frac{p}{p-f} = \frac{30}{30-15} = 2$ that is to say, the volume is doubled.

" If the temperature is 203° F., $f=25$ is sextupled.

" If $p=60$ inches, $f=30$ inches, at the temperature of boiling water, then the space is equal

to $\frac{60}{60-30} = 2$; that is to say, water at a pressure

of 60 inches of mercury and at the temperature of boiling water produces a vapour which is exactly double that of the volume of the air.

" If ether is used: let the temperature be $=70^{\circ}$ F. (17° R.), we shall have $f=15$; if we suppose $p=30$, in that case the volume of air will be doubled."

239. Dalton also examined the different opinions respecting the relations of two gases which occupied the same space together; the following is that which he adopts.

" The particles of one of the two fluids cannot exercise either attraction or repulsion on those of the other; that is to say, in this supposition, they will conform to the laws of elastic bodies.

" In that case, if the two fluids are mixed, they will distribute themselves so that their united forces shall equal the pressure of the atmosphere. Each of them, with respect to the other, will be only an obstacle which will occupy the space left vacant between the homogeneous moleculæ; the pressure exercised on a given molecule of a mixt fluid thus composed, will proceed exclusively from the repulsive action of the homogeneous moleculæ.

" The author is of opinion, that this hypothesis resolves all the difficulties in the mixtures of gases without combination. Thus all the components of the atmosphere, oxigen gas, azote, hidrogen, carbonic acid, aqueous vapour, &c. are arranged together, at a given pressure and temperature; and by a paradoxical, though true, disposition, each of them occupies all the space destined for the aggregate of these fluids. Besides, they are so rare, that the space which encloses the whole of them differs very little from a vacuum.

" Independently of the azote and oxigen gases, the two principal components of atmospheric air,
the

the author considers the aqueous vapour and carbonic acid as two other ingredients constantly mixed in this fluid. He assigns the following proportions to these four substances.

"The azote gas would, alone, sustain 21.2 English inches of mercury in the barometer.

"The oxigen gas would sustain about 7.8: neither of these gases change their state by any known degree of cold.

"The aqueous vapour varies in quantity, according to the temperature."*

240. Thus two elastic fluids, of different natures, exercise no more reciprocal action than if one was a vacuum with respect to the other: that which occupies the first space is considered as an obstacle, which is only made known by an inaccurate comparison of which I shall speak, but which does not act on the expansive force of the gas, and which does not exercise chemical action, and only a momentary existence is assigned to this obstacle.

Deluc, to whom so many laborious and important researches on this subject are owing, at first, attributed all the phenomena of evaporation solely to the action of fire; he afterwards admitted † a

* The paper from which Pictet appears to have extracted this account for the *Bibliotheca Britannica* is inserted in Vol. V. p. 244, of the Quarto Series of Nicholson's *Philosophical Journal*. In it Mr. Dalton states the power of the carbonic acid gas to be equal to $\frac{1}{2}$ inch. T.

† *Philos. Trans.* 1793.

force,

force, which he compared to that of capillary tubes, which introduced the moleculeæ of one elastic fluid between those of another, until there was an equilibrium between the action and the reaction, which, at the bottom, is another manner of describing affinity: but neither him, nor the philosophers who have followed his opinion, imagined that one gas was to be considered as deprived of mechanical action, or as a vacuum in respect of another. This opinion, which is rendered important by well selected and very interesting results, must therefore be opposed by new observations.

I shall in the first place remark, that in the hypothesis which I have chosen, that is to say, in admitting that, by the action of a gas, the elastic vapour takes the properties of a permanent gas, the phenomena which have just been described are explained in a natural manner: I take as an example the case in which the elastic tension of a liquid being 15, and the pressure 30, the liquid is contained in a space with a volume of air, and produces the manometric effects, (166), and in which the compound gas afterwards passes to the state which it wóuld have in the atmosphere, at a pressure of 30, and still in contact with the liquid; the air in the manometer experiences a pressure of 45 degrees, its volume will therefore be diminished in the proportion of 45 to 30, but it will also be dilated in the same proportion when it passes to a pressure of 30: the elastic vapour must experience a similar dilatation, and acquire a correspondent specific

specific levity; but the volume being augmented by the dilatation of the air, a new vapour will be formed corresponding to the augmentation of the space: the result of these three causes united will give a volume precisely double that which the air had; in fact, if dry air at a tension of 30 is introduced into a space in which it can dilate, and if a liquid at a tension of 15 is placed therein, it follows from the principles established by observation, that the elastic vapour which forms is in the same quantity in a space which is void or which is filled with air; that the vapour will occupy half the space in which the air was contained, half of this must therefore be driven out; but it will require a new space, equal to that of the first half, and which will be in the same situation; a quantity of vapour will therefore be formed equal to the first, and the volume will be doubled conformably to the formula of Dalton.

Nevertheless, it is not a matter of indifference, as will be seen shortly, to prefer a physical hypothesis which accords with the properties from which the phenomena are derived, to another which can only represent their results: I shall therefore examine the supposition on which Dalton founds his explanations.

1st. It is not essential to the gases to be deprived of reciprocal action: do not nitrous gas and oxygen gas; ammoniacal gas and muriatic gas; oxygenated muriatic gas and sulphurated or phosphorated hydrogen gas, enter into combination

tion with each other, or are they not very easily decomposed by their reciprocal action?

2d. Hidrogen gas and oxigen gas form water in a given circumstance; azote gas and oxigen gas can also produce nitric acid; but the reciprocal action which decides the combinations cannot be considered as a force commencing at the precise moment at which it is manifested, it must have existed long before producing its effect, and increases gradually until it becomes preponderant.

3d. Azote gas comports itself with oxigen gas, in the changes occasioned by temperature and pressure, precisely like one and the same gas: Is it necessary to have recourse to a supposition which obliges us to admit so great a difference of action without an ostensible cause?

4th. When one gas is mixed with another which has a great difference of specific gravity, for example, when hidrogen gas is placed above carbonic acid gas, it is not until after several days that the mixture becomes uniform: if the first only offered a void space to the carbonic acid, it would rush into it with rapidity; will it then be said, that hidrogen gas offers an obstacle which must be overcome? If this obstacle is a mechanical force, the elastic action must become more powerful than it; but then each gas will continue to act reciprocally by their elasticity.

5th. If a gas offered to a forming vapour only spaces which were to be considered as empty, and if

if it opposed no other resistance to it but such as might be compared to that of gravel, which suffers water to pass through its interstices, it could only retard the formation of the vapour, as is asserted; but the volume which it occupies does not change, and nevertheless that of the vapour is wholly added to it; it is said that it then dilates, because it sustains a smaller proportion of the pressure. Is such a division of the same pressure of the atmosphere analogous with any physical property yet known? Can it be conceived, that an elastic substance exists, which adds its volume to that of another, and which nevertheless does not act on it by its expansive force?

241. That which has led Dalton to reject a chemical affinity between the gases, is, that, in the action of the affinity, there is *reciprocal penetration, disengagement of caloric, change in the densities, and that the phenomena are essentially different from those of a simple mixture.*

These effects of affinity cannot be disputed, when it is sufficiently energetic to produce them, or when they are not concealed by contrary effects; but it frequently happens that its action is too weak to cause a change of dimension or of temperature, or perhaps more powerful causes may only permit contrary effects to appear.

Mercury which adheres to the surface of a metallic mass, exercises an action there, and yet it produces no change in the dimensions: if the cohesion

hesion was not opposed to it, it would completely dissolve the metal by the same force as causes it to adhere to its surface.

A salt is dissolved in water only by a chemical action, yet so far from this producing a diminution of volume, there is a dilatation, and instead of a disengagement of caloric there is an absorption, (142).

This solution of a salt is strongly analogous with that of a liquid by the air: only a determinate quantity of salt dissolves at a given temperature; if the quantity of the water, and consequently its volume, is diminished, a portion of salt corresponding to that diminution is deposited, the force of cohesion then produces that which the disposition to liquidity occasions in the solution of a liquid by a gas; heat also causes an analogous effect in both: the comparison of these solutions made by Leroi would have been exact, if he, like Saussure, had taken into the consideration, the gazeity acquired by the liquid in taking the state of vapour.

242. Dalton denies the assertion of Lavoisier, that atmospheric pressure alone, retains water in the liquid state at the common temperature. "If," says he, "the aërial atmosphere was at once annihilated, leaving only its aqueous portion, this would be but little augmented, because it already exists in the air nearly at a maximum of that which the temperature can produce and support:

" support: the suppression of the obstacle will
" only accelerate the evaporation, without sensi-
" bly augmenting the absolute quantity.

" This notion, that the pressure impedes the
" evaporation of liquids, a notion which is taken
" as an axiom among modern philosophers, has
" perhaps produced more error and perplexity in
" the science than any other opinion equally ill-
" founded."

This observation of Dalton does not appear to me to be just, and he seems to be led, by a consequence of his opinion, into a false idea of the quantity of vapour which would be formed by the suppression of the atmosphere, and of that which can dissolve in the atmosphere.

In his examination of the effects of the pressure of the atmosphere, opposed to the action of caloric, Lavoisier remarks,* that *without it the molecule would be infinitely dispersed, and that nothing would limit their separation, unless their own weight should collect them to form an atmosphere.*

He afterwards describes the observations he made with La Place on the vaporisation of ether and of alcohol in a vacuum, and on the elastic force of vapour which increases according to the temperature, and which reduces the liquid into elastic fluid, whenever its tension becomes greater than the pressure of the atmosphere: I see nothing

* *Traité Elém. de Chim. I^e Part. p. 8.*

in these ideas which is not conformable to the phenomena.

In fact, if distillation is performed without the access of air, and if by cooling the recipient, the cold suppresses the greatest part of the resistance of the elastic vapour, which by that means continues to be produced and to condense, it verifies the principle, that without the pressure of the aërial atmosphere, or of that which forms, liquids would pass to the elastic state.

Observation has shown that the quantity of elastic vapour, in a vacuum, or in the same space filled with air saturated with humidity, at the same degree of temperature, is the same; hence we may conclude, that the quantity of elastic vapour which forms in the atmosphere is different from that which would be produced if the atmosphere was suppressed: in the first case, supposing a uniform degree of temperature, the quantity of water contained in the same space at the superior or at the inferior part of the atmosphere would be the same, independently of the difference of pressure; at least this effect would take place until the chemical action of the air became inferior to the effect of the weight of the vapour itself. The diminution of pressure would only act on the quantity of air which would be diminished by it, while that of the elastic vapour would remain the same; thus, a cubic foot of air at a pressure of 14 inches would have but half the quantity of air which it would at a pressure of 28 inches, but the quantity

quantity of water would be the same at the same temperature and at the same degree of saturation; whence it results, that the variations of the barometer occasioned by those of the humidity of the atmosphere may be much greater than was believed by Saussure, § 228, and Deluc.*

In the second case, only a quantity of vapour determined by its weight, would be formed; thus, at 10° of the thermometer, the quantity of vapour spread through the whole atmospheric space would not surpass that which is equal to the weight of 0.4 inch of mercury.

As the quantity of water which can be held in solution by the gases is the same in all, and as it is proportionate to their volume and their temperature, the state of desiccation and of humidity can produce considerable variations in those which have little specific gravity: thus, when hydrogen gas at 10° is saturated with humidity, the water which it holds in solution forms nearly a tenth, and at 16° it makes near a sixth.

243. It is to the property possessed by the gases of dissolving water, that evaporation is owing: a volume of dry air requires the same quantity of water for saturation which, in a vacuum, would fill the space occupied by the saturated air: thus it receives an increase of tension equal to that of the vapour; the only difference is, that the evaporation will be more rapid in the vacuum; but it

will stop when the formed vapour has acquired that tension which it could not exceed at a given temperature; the air, on the contrary, by being renewed, presents new spaces to receive the water, so that the total effect of the evaporation is much greater, and it is so much the greater as the air is more distant from the degree of saturation, and more heated: it is obvious, that while the circumstances are unchanged, the quantities of liquid which evaporate will be proportionate to the tension determined by the temperature. Dalton has not only confirmed, by very interesting experiments, the relation of the quantity of a liquid which is evaporated at different degrees of temperature, with the tension which it has at these degrees, but he has also shown that liquids, such as water, alcohol, and ether, only differ from each other, in this respect, by their distance from the point of their respective ebullition, so that at the same distance from this term the quantity of their evaporation is equal.

When once water has arrived at ebullition, its vapour only mixes with the air like a gas, while it retains its temperature; but it resumes the liquid state either by an augmentation of pressure, the temperature remaining the same, or by being cooled, without an alteration in the pressure.

Dalton proved that the vaporisation produced by a heat maintained at the *minimum* requisite for ebullition, may be augmented by the agitation of the air; which shows that then, in addition to the vaporisation,

vaporisation, the air also acts by its dissolving action, and that consequently the result is compounded of evaporation and vaporisation, but it is probable that when the ebullition is strong, the air is incapable of acting by its contact, and that then the effect is entirely due to the vaporisation.

244. Distillation partakes of the effects of vaporisation and evaporation, according to the degree of temperature.

If the liquid distilled is in a state of ebullition, vapour is formed ; when the tension has become equal to the pressure of the atmosphere, it drives off the air in the recipient, and being condensed by the cold, gives place to the new vapour.

If the heat is inferior to that of ebullition, the liquid does not acquire a tension which can counterbalance the pressure of the atmosphere : unless therefore the distillation is performed in an exhausted apparatus, no vapour will be formed but by the intermedium of the air, and a current must be established to accomplish the distillation ; the air, which will acquire a greater tension by the accession of vapour, will dilate and drive before it the air which has not received any vapour ; a current will be established which brings back the air that had been obliged by the cold to abandon part of its vapour, as we have seen that there is one produced in the solution of salts.

Fontana has published some curious experiments, which prove that the expulsion of the air,

or the circulation of that which holds the vapours in solution, is necessary to the accomplishment of the distillation,* even at a degree of ebullition which does not then exist.

He made a communication between two matrasses by means of a tube hermetically sealed ; in one of them he put water, and exposed it for a long time to the heat of ebullition, without producing distillation : ether was kept for twenty-four hours at a heat equal to 50° R. while the other matrass was surrounded with ice, and, in like manner, distillation did not take place. The pressure resulting from the first effect of the vapour which is dissolved, opposes the production of any more : but if the space was empty, distillation would take place at the lowest temperature, as was remarked by Saussure.

Fontana concludes from his experiments, that evaporation is not owing to the sole action of fire on a liquid ; *for if this was the case, the water would penetrate through the air, although inclosed, as is done by all the other bodies which any impulse whatsoever directs against this latter fluid.*

Dalton is of opinion, "that the presence of the atmosphere is an obstacle, not to the formation, but to the diffusion of the vapour, a diffusion which would take place instantaneously, as in a vacuum, if the moleculæ of the air did not

* Journ. de Phys. 1779.

" oppose

" oppose it by their inaction. This obstacle is
" taken away in proportion to the absolute force
" of the vapour: it does not proceed from the
" pressure or the weight of the atmosphere, as has
" been hitherto supposed; for if it were so, no
" vapour could be formed below the degree of
" ebullition: but it is an adventitious obstacle
" analogous to that experienced by a current of
" water which descends through gravel."

The editor, whose opinion, which had been some time published, Dalton has adopted in this respect, adds, "the comparison would have been still more just, by supposing that the water, in rising to regain its level, passed through a bed of gravel: the pressure of the gravel is entirely supported by its base, and the water, which in ascending distributes itself among its interstices, experiences no effect from it: it is solely obstructed in its ascent according as it finds more or less room to lodge in."

In Fontana's experiments all the space is occupied by the gravel: there is not only an obstacle to the diffusion, but also to the production of the vapour.

Can the obstacle opposed by hard and inflexible moleculeæ to the passage of an incompressible liquid, be compared to that of elastic moleculeæ? Must not this mutual obstacle prevent the expansive effort of both? From this itself an elastic fluid cannot be the same in a vacuum in comparison with another, after diffusion, and the participation

pation of a common pressure between them is a gratuitous supposition.

If one gas occupied the interstices of another, as though they were vacancies, there would not be any augmentation of volume when aqueous or ethereal vapour was combined with the air, nevertheless there is one proportional to the quantity of vapour added: humidity should increase the specific gravity of the air, whereas it renders it specifically lighter, as has been already noticed by Newton. A table in which Dalton has pretended to show how different gaseous moleculeæ may be disposed in the same space, is therefore only a picture of the imagination.

245. All the liquids have the property of dissolving in air; all have a greater or less tension in a vacuum; but the phenomena are changed when two liquids exercise a mutual action, whether both are in a liquid state, or one is in that of elastic vapour.

Concentrated sulphuric acid does not appear to dissolve in humid air, but it robs it of the humidity which it shares according to the force it exercises on the aqueous vapour, and according to the dissolving force of the air: these two forces may be in equilibrio, but it is easily destroyed by a trifling difference in the temperature, so that the acid which, at one temperature, takes the water, yields it at another: it appears that it is only when the air is very dry and the acid greatly concentrated, that this can act by its tension,
and

and dissolve in the air in the ratio of that tension.

An analogous effect is produced when two liquids, unequally evaporable, are submitted to distillation, for example, water and sulphuric acid: when the proportion of the water is great, it at first passes alone, but a smaller quantity comes over than would if it was unobstructed; its tension is diminished by the effect of the action which the sulphuric acid exercises upon it; the term of its ebullition is protracted, as we have seen it was by muriate of lime in Dalton's experiments. At length it reaches a term at which the tension acquired by the sulphuric acid from the heat overcomes the action by which it tended to retain the water; then the latter communicates part of its volatility to it, and produces an effect contrary to the preceding: the sulphuric acid passes therefore in a greater quantity, at a given heat, than if it had been deprived of water.

This effect of the mutual action of two liquids is also observable when two liquids of different evaporability are subjected to experiment in the vacuum of the barometric column: a mixture of ether and alcohol depresses this column less than ether alone.

If therefore a mixture of ether and alcohol is submitted to distillation, a more elevated temperature is required to produce the same effect on the ether than if it was alone; as soon as it passes in the distillation, its vapour not only permits the alcohol

alcohol to furnish its part in the ratio of its own tension, but it advances the term of its ebullition, and the quantity of alcohol which passes with it is greater than if it was only subject to the tension it would have had at the same temperature; whence it results, that ether absolutely deprived of alcohol cannot be obtained by distillation, unless a substance is added, which, by its action, retains the alcohol.

This is done by means of water, whose action on ether is very weak, but much more energetic on alcohol; hence it arises, that if common ether, containing alcohol, or a liquor more soluble in water than the ether, is passed into the barometric vacuum, its tension augments on introducing a little water, in the same manner as if an alkali is added to sulphuric acid which retains water: it is thus that a fixed base re-establishes the elastic property of one which is volatile by dividing the action it exercised on an acid, (150).

This action of water on ether has been considered as a phenomenon irreconcileable with the laws of the dilatation of vapours;* but having engaged Gay Lussac to examine this subject, he easily elucidated it; and has transmitted me the results of his experiments in a note which I subjoin. (*Note XVII.*)

* Ann. de Chim. tom. XLIII.

CHAP. II.

Of the elementary Parts of the atmospheric Air.

246. THE air contributes to so great a number of chemical phenomena, by the combinations which it forms, that it is important to have a precise idea of the parts which compose it; of the proportions in which its elements are found, either in the natural state, or in the different products of chemical operations; and of the methods by which these proportions are determined.

The oxygen gas and azote gas which enter into the composition of atmospheric air exercise only that mutual action which produces the species of combination which I have particularly distinguished in the elastic fluids by the term solution, and which does not affect the dimensions peculiar to each species of gas.

This action is sufficient to overcome the resistance offered by the specific gravity, so that an elastic fluid resulting from different gases which are mutually dissolved, has a uniform specific gravity, determined by the proportion of the gases, and by the pressure they experience at a certain temperature: hence it arises, that, even on the summit of Mont-Blanc, atmospheric air contains carbonic

carbonic acid,* and probably in the same proportion as at the level of the sea: nevertheless the difference of specific gravity may limit the quantities which can dissolve; this may explain the greater proportion of azote which is admitted, according to the observation of Saussure, at the height of the elevated summits of mountains; yet the observation of this celebrated philosopher is subject to some doubts, founded on the inaccuracy of the eudiometric means which were at that time adopted with so much confidence, and his son, who follows his footsteps with such success, has himself confirmed these doubts by the observations he has since made; besides the differences indicated were very trifling, and established on a small number of observations which were not even certain, and similar variations are found between the air of Geneva, and that of the plains of Piedmont; now we shall see how doubtful this latter difference is.

In the simple solution of water and the other liquids by the air, this acts on the vapour as on a gas, without experiencing any change in its own proportions; but water which dissolves it, and which acts in a much greater mass, seems partly to effect this decomposition, for that which is exposed openly to the atmosphere, absorbs an air which is purer, or in which the proportion of oxygen is greater than in atmospheric air, and

* Voy. dans les Alpes, tom. VIII. edit. in 8vo.

when

when it holds azote gas in solution, it abandons a part to take the oxigen gas in its stead: hence it arises, that oxigen gas is changed by long exposure above a considerable quantity of water, unless the light obliges it to preserve its elastic state, or restores it to it.

247. Some substances exercise a much more powerful action on oxigen gas, and form intimate combinations with it by overcoming both the force of its elasticity and the action of azote gas.

This property, which is possessed by several substances, of abstracting the oxigen gas from atmospheric air, and leaving the azote gas in the elastic state, has been used to determine the proportions of azote gas and oxigen gas which form the atmosphere, or which enter into the products of chemical operations: the name of eudiometers has been given to the means which have been employed, and under this denomination is comprised both the substance which combines with the oxigen, and the apparatus used to measure the effect it produces: but chemists are not agreed in the choice of these means, or on the consequences which should be drawn from them.

Eudiometers may be distinguished into two species: in the one, a determinate volume of a gazeous substance is made to act on a volume of atmospheric air which is also known; a part of the gazeous substance, by uniting with the oxigen of the atmospheric air, forms a combination, soluble in

in water, and whose volume is absorbed by it ; the diminution will be greater as the quantity of the oxygen is more considerable : by this means, therefore, the quantities of oxygen in different gases might be compared, if they were proportionate to the diminutions ; but it is not calculated to ascertain the absolute quantity of oxygen, unless the proportion in which it combines with the gaseous substance which loses the elastic state with it, is exactly known.

In the second species of eudiometer the oxygen combines with an oxygenable substance, solid or liquid ; the residue is then pure azote gas, or at least such as has experienced no change from the combination but what can be estimated, and thus the absolute quantity of the two parts of atmospheric air is immediately ascertained. This consideration seems to indicate that the latter method should have the preference ; let us, however, examine more minutely the advantages and inconveniences attendant on each of them.

248. We are indebted to Priestley for the ingenious idea of measuring the purity of the air by the diminution produced in it by nitrous gas, and it has since been ascertained that this diminution depends on the proportion of oxygen gas which it contains. Fontana contrived an apparatus for performing this experiment with accuracy, and the process has ever since been generally known by the name of Fontana's Eudiometer.

This eudiometer has the disadvantage of giving considerable

considerable variations in the results, according to the agitation, the temperature, the proportion, the qualities of the water, and the dimensions of the apparatus; as was remarked by Fontana, and in a more particular manner by Ingenhouz: Cavendish endeavoured to prevent these causes of uncertainty by admitting the nitrous gas into the air by single bubbles, and by establishing a perfect equality in every part of the process; * but it may be concluded from his observations, that, without attending to all the circumstances, as he did, no comparative result can be obtained from these experiments: hence much uncertainty and contradiction is found in the observations which have been made by it.

Cavendish in particular has ascertained correctly some of the causes which produce a variation in the results; according to his observations, when the jar, in which the mixture of nitrous gas and air is made, is undisturbed, the diminution is slower and weaker than when it is agitated; the difference is as 99 to 108: that which arises from the time required to introduce one gas to the other by bubbles, is still greater; the diminution produced by distilled water is greater than by that not distilled, and water which has been in contact with nitrous gas produces less than that which has not; if the water contains oxygen it occasions a greater diminution than that which has been some

* Philos. Trans. 1783.

time in contact with azote gas; when the air is passed into the nitrous gas the diminution is greater than by the reverse process, in the proportion of 108 to 90. We shall presently examine the cause of these differences.

It is worthy of observation, that the diminution was not sensibly varied in Cavendish's experiments, whether the nitrous gas was impure, or whether it was free from mixture, provided a sufficient quantity was employed: Fontana had before noticed the same circumstance. This shows the inutility of the rules prescribed by Humboldt to determine the quantity of azote gas which he supposed was always found in nitrous gas, with a view to deduce the proportions of oxigen and nitrous gas which combine and produce the diminution: the azote gas is separated by means of the sulphate of iron, as he has pointed out, but its existence in the nitrous gas is accidental and foreign to the absorption.* The accurate experiments of Davy have shown that nitrous gas, extracted by a process similar to that of Humboldt, leaves scarcely any residue when it is submitted to the action of sulphate of iron, an experiment on which Humboldt depended to prove the co-existence of azote: its absorption is also nearly complete by oxygenated muriatic gas.†

Among the observations of Cavendish there is

* Ann. de Chim. tom. XXVIII.

† *Ibid.* tom. XXXIX.

one, the true explanation of which could not be shown at the period in which he made it: he found that while nitrous gas, extracted by means of mercury, of copper, or of brass, produced equal diminutions, that which he formed by means of iron indicated a greater diminution, although when it was employed in a small proportion, the diminution was less: it appears to me that these effects depend on a portion of gaseous oxide of azote which is united to the nitrous gas produced by the iron, and is absorbed by the water without acting on the oxigen gas, while that produced by the other methods indicated, is free from it.

If the results which are obtained by carefully avoiding all the causes of error are comparable with each other, this is not the case with those of the experiments which are not made with the same care and with the same skill. Besides, they cease to be so with respect to the very different proportions of oxigen and of azote; for Humboldt himself has observed that oxigen gas when insulated produces a diminution proportionally greater than when it enters into the composition of atmospheric air.

Finally, this method, by which different airs may be compared, by carefully attending to the circumstances, does not show the proportion of oxigen and azote in the air which is examined, or if a conclusion is expected from it, new causes of uncertainty are met with, and the data which are adopted can only be serviceable in the method which

which is employed, since the diminution of the volume varies, as we have just seen, according to the circumstances of the process.

249. The experiment which is made by the combustion of hidrogen gas, and which is known by the name of Volta, to whom we are indebted for the apparatus with which it is executed, has much more precision than the preceding, and has the advantage of showing the proportion of oxygen gas which is reduced into water, by the correct determination of the proportions of water, which has been obtained in operations made on large quantities, and with all the accuracy that chemical experiment is capable of.

It is difficult to conceive why so much care has been bestowed in bringing to perfection the use of nitrous gas, in which so many causes of error are discovered, and from which the proportions of oxigen gas cannot be ascertained, while a method was possessed which has the double advantage of having less uncertainty, and showing the proportions.

Nevertheless Volta's eudiometer, which has great precision with oxigen gas, containing but a small quantity of azote gas, has the inconvenience of not producing the combustion of all the oxigen gas, when it is blended with a large quantity of azote gas, as it is in atmospheric air; neither will the inflammation take place if there is only a small proportion of oxigen gas: this latter inconvenience may be guarded against by adding a known quantity

quantity of oxigen gas, which determines the combustion of that which pre-existed, and by dividing the result: nevertheless there is always a portion of oxigen gas which escapes combustion, as is shown by the residue obtained in Monge's process for the formation of water; for this residue contains oxigen and hidrogen gases which have resisted the combustion, because they were mixed with too large a quantity of azote gas and carbonic acid gas.

250. A great number of substances have the property of combining with oxigen, without causing the disengagement of any gas, and without absorbing azote gas, they are consequently serviceable to determine the quantity of oxigen in any gas; but those must be chosen which act so forcibly that the absorption need not be of long duration, and that they are capable of taking all the oxigen from the azote which tends to retain it by an increasing force: these eudiometric processes have the advantage of indicating directly the proportion of oxigen in any gas whatsoever, provided it is simply dissolved in it: let us now inquire what the preference is which some of them merit.

The alkaline sulphurets dissolved in a small quantity of water, appear to me to have this property in a high degree, and require only a very simple apparatus; a tube accurately graduated is sufficient. The mixture of sulphur and iron-filings acts with more promptitude, but there are

two causes of uncertainty in its action: when the oxigen gas is absorbed, sulphurated hidrogen gas may be disengaged, as was shown by Priestley, or perhaps these two effects are simultaneous, and to this cause Macarty attributes* the smaller diminution he obtained by employing this mixture, than when he used an alkaline sulphuret: in the second place, a little ammonia is produced, as appears from the observations of Kirwan and of Austin. It was probably this cause which augmented the diminution in the experiments of Scheele, who pointed out this eudiometer, and who concluded from his experiments that atmospheric air contained 0.27 of oxigen gas.

An alkaline sulphuret dissolved in a small quantity of water has not these inconveniences; as soon as the oxigen gas is absorbed its action ceases, and the residue does not experience any further diminution, which proves that it has no action on azote; nevertheless Macarty is of opinion that the sulphuret absorbs a portion of azote, and that it is not until after being saturated with it, that its action is limited to the condensation of oxigen gas: he even asserts, that he obtained the absorption of half the azote contained in a small volume of atmospheric air, by fresh-made sulphuret of lime. For my own part, I have not observed the smaller difference in the diminution produced by a recent sulphuret, or by the same

* Journ. de Phys. tom. LII.

sulphuret which had been agitated in atmospheric air; but I have only made experiments with the sulphurets of pot-ash and soda, these latter sulphurets may therefore be employed without any fear of error.

The alkaline sulphurets have nevertheless the inconvenience of requiring a long time to complete the operation, which must be prolonged to be certain that it is terminated, because no other index but the diminution of the volume of the gas can announce its end: but it may be shortened by agitation.

251. Phosphorus, for which Achard, Reboul and Seguin, have contrived apparatuses, produces its effect instantaneously by its vivid combustion, but its action is tumultuous and may easily lead to accidents.

The slow combustion of phosphorus has the advantage of being much more expeditious than the action of the sulphurets, and of showing the completion of the operation, because the cloud which accompanies it, and which is luminous in the dark, disappears; but while the phosphorus absorbs the oxygen, the azote dissolves the phosphorus, or rather the oxygen combines successively with the phosphorus which had been dissolved by the azote, and the latter remains saturated with the phosphorus which had taken the elastic state, from whence results an augmentation in the volume of the azote: this augmentation is of no consequence, if the object be the simple comparison of two airs,

but it requires to be corrected, if it is desired to ascertain the quantity of oxigen gas, by that of the residue; experience has taught me that $\frac{1}{45}$ of the volume of the latter must be subtracted.

Davy has proposed another eudiometric process, which is sulphate or muriate of iron impregnated with nitrous gas*; this solution, particularly that with the muriate of iron, effects the absorption of the oxigen gas in a few minutes; but he observes that the instant of the greatest diminution must be seized, because the nitrous gas is partly decomposed, and, as the salt of iron becomes more oxidized, both nitrous gas and azote gas are disengaged.

252. To obtain a thorough knowledge of a great number of phenomena, it is important to ascertain, with all the precision that can be attained, what the proportions of oxigen and azote are, which enter into the composition of the atmosphere, and what variations they are capable of: the chemists, who at first flattered themselves with being able to compare the vital properties of atmospheric air, have been much employed in this investigation, and although they soon lost the hopes they had conceived relative to the salubrity of the air, they have believed they discovered a variation with respect to places, and to the meteorological disposition: they have announced sen-

* Bibl. Britan. tom. XVII.

sible differences at a few hours interval, or at a few paces distance.

Nevertheless Cavendish, by an attentive consideration of all the circumstances of the proof by nitrous gas, pointed out, as early as 1783, that the proportions of the two elements of the air were invariable, notwithstanding the distance of places, and the difference of the temperature: the observations made by Macarty, in Spain, have confirmed the opinions of Cavendish. I was at Cairo at a season when Reaumur's thermometer usually exceeds 30°, and when the air is liable to be affected by a great inundation: I could only oppose the prejudices of which I partook by the observations I made, for I had lost sight of Cavendish's experiments and was unacquainted with those of Macarty: my observations led to the same results, and have been confirmed by those made since my return.*

The experiments of Davy, pursued under different circumstances, and the examination of some air sent to Beddoes from the coast of Guinea, have also proved that no sensible difference is to be found in atmospheric air, with respect to the proportions of its elements.

It appears, therefore, that it is solely to the uncertainty attendant upon the action of the nitrous gas, which has been principally employed in eudiometric experiments, that the differences in the

* Mém. sur l'Egypte.

proportions

proportions of oxygen gas, which have varied between .20 and .30, are to be attributed.

Macarty, who employed a sulphuret, fixed the proportion of oxygen between .21 and .25: the proof by Volta's eudiometer only gives .20 nearly; but Volta did not attend to those variations, which were found by employing nitrous gas: I attribute the small difference between his eudiometer and the action of sulphurets to the portion of oxygen gas which escapes combustion.

A multiplicity of experiments which I have made with every possible accuracy, seem to prove that the true proportion of oxygen gas is .22 and a fraction; the experiments I made in Egypt gave me nearly $\frac{1}{10}$ more of azote, and I have explained this small excess in the residue by the water which the air might hold in solution at the high temperature in which I operated: perhaps it might only be occasioned by a trifling inaccuracy in the graduation of the tube.

Davy only makes the proportion of oxygen to be .21, but he observes that the alkaline sulphurets produced a little greater absorption. I attribute this slight difference to the disposition of the nitrous gas to take the elastic form; for he observes that this gas is disengaged from the solutions of iron, in a vacuum; it will therefore, dissolve in the azote gas, and by that means the volume of the residue will be a little augmented: this appears to be a disadvantage in this species of eudiometer, when great precision is desired.

If

If the process with the sulphurets and with phosphorus appear to be a little more accurate in determining the proportions than Volta's eudiometer, this appears to have the advantage when employed in the inverse process by which hydrogen gas is examined by oxygen; and it is frequently serviceable, in the inquiries into the composition of gaseous substances which are still necessary, to employ these two methods alternately.

Atmospheric air always contains a certain quantity of carbonic acid, and we have seen that Saussure found it on the summit of Mont-Blanc: the quantity is estimated at .01, but it appears that this estimate is much too large.

Besides the parts which are constant, atmospheric air may hold different substances in solution, which take the elastic form in it, and of which some are the principle of odours; but hitherto these emanations have escaped chemical means, which can destroy some, but not point them out: Cavendish has already shown that no difference is found in air which has been in contact with odiferous flowers, or with substances in putrefaction.

(*Note XVIII.*)

CONCLUSION

CONCLUSION

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FIRST PART.

253. TWO species of affinity have been admitted as causing the effects arising from the mutual action of bodies, and particular laws have been attributed to that which was particularly considered as chemical: in Saussure's Essays on Hygrometry, I find a correct exposition of the properties which I have deemed satisfactory in the explanation of all the phenomena produced by this action, as well as of the distinction which it has been thought necessary to establish between them.

" Different bodies have a different fitness to " receive the vapours contained in the air, and they " charge themselves with them in the ratio of their " affinity with these vapours, or with the water of " which they are formed.

" Expose equal quantities of salt of tartar, quicklime, wood, linen, &c. in the same air; let all these bodies be as perfectly dry as possible; some of them will imbibe water, and increase in weight, but in unequal quantities: the salt will " tak

“ take more than the lime, the lime more than the wood, and the other bodies will not take any.

“ Now these differences can only proceed from different degrees of affinity in these bodies for the water; for they are not dependent on the form, nor on the volume of these bodies, nor even on the nature of their aggregation, since bodies already liquid, such as vitriolic acid, attract the water contained in the air with the greatest force. An additional proof that this absorption of vapours depends on affinity is, that the union of the condensed vapours with these bodies is really that which results from a chemical affinity: this water is in a state of combination with them, it cannot be taken from them by any mechanical means; it is intimately united with their elements; chemical means alone can separate it from these bodies by offering it combinations to which it tends with a more powerful affinity.

“ Other circumstances being equal, the affinity of these bodies with water, is greater in proportion as they contain less of it, or, if the expression be admitted, as they are more strongly dried.

“ The fixed alkali, perfectly desiccated, attracts the humidity of the air with an extreme force; placed in the pan of a balance, its weight is seen to augment sensibly from one minute to another; but in proportion as it drinks the vapours, its thirst, or its attractive force diminishes, and at last,

" last, its weight only increases by insensible degrees.

" It is the same with the other chemical solvents; they act at first with the greatest celerity and with the greatest force, and their activity diminishes in proportion as they approach the point of saturation; but there is this particularity in the affinity which exists between the vapours and those bodies which absorb them, or " *hygrometric affinity*, that not only their activity, but even the degree of their affinity diminishes in proportion as they approach the term of saturation. Thus, even though a body has but little affinity for water, this defect may be compensated by a greater desiccation; and, on the other hand, that which has the most, falls to the level of that which has the least, when it comes much nearer to its point of saturation.

" I enclose one or two ounces of a fixed alkaline salt, very caustic and very dry, in a globe containing four cubic feet, filled with air moderately humid, but without any superabundance of humidity: this salt absorbs 24 or 25 grains of water which it draws from these four cubic feet of air. Then the salt, by having imbibed this water, has lost a little of its attractive force and, in return, that of the air is so augmented by the loss it has sustained of these 24 grains of water, that although it contains more, the salt cannot abstract it because the air retains it with a force equal to that with which the salt demands

“ mands it ; and this is not because the salt is
“ saturated, or nearly so, for in an air which is
“ humid and renewed, it could still absorb two
“ hundred times as much, but because this quan-
“ tity, notwithstanding its smallness, has dimi-
“ nished its absorbent force. In fact if two more
“ ounces of the same salt, perfectly dried, be intro-
“ duced into the same globe, they will still ab-
“ stract some portions of humidity from the air
“ inclosed with them, and so on successively until
“ the extreme desiccation has brought the attract-
“ ive force of the air into an equilibrium with
“ that of the fixed alkali.

“ This species of affinity differs therefore in this
“ respect from the other chemical affinities, of
“ which the nature or the degree does not change
“ on approaching saturation; for if several menstrua,
“ whose affinities for any body are unequal with
“ respect to each other, are on the point of acting
“ at the same time on it; the most powerful will
“ begin by attacking this body, and although it
“ proceeds continually towards saturation, the
“ superiority of its forces over those of the other
“ solvents, will not be diminished on this account;
“ it will not suffer any thing to be dissolved
“ by the other menstrua before it is completely
“ saturated; or if, at first, it has been deprived of
“ some portions of the dissolving body, it will
“ resume them until its complete saturation. If,
“ for example, chalk is projected gradually into a
“ mixture of vitriolic acid, nitrous acid and vine-
“ gar,

" gar, the vitriolic acid must be completely saturated with the chalk before the nitrous acid and " vinegar can obtain an atom; afterwards the nitrous acid must be saturated; and, finally, the " vinegar will not take any until after the perfect " saturation of the other two.

" On the contrary, if, in a given space, there is " not a sufficiency of water, or of vapour, to saturate all the bodies confined within it with humidity, none of them will be completely saturated; " all will have a little: the water will be divided " between them, not, indeed, in equal parts, but in " quantities proportional to the degree of affinity " of each of the bodies with it. Those which attract it most forcibly will take that quantity " which will reduce their attractive force to the " level of those whose attraction is least, and thus " a species of equilibrium will be established between them.

" This partition is made by the intermedium of " the air, which takes from those which have too " much, and gives to those which are deficient, " retaining at the same time that part which corresponds with the degree of its own affinity for " water.

" If, when this equilibrium is fully established, " new vapours, in a quantity insufficient to saturate both the air and the bodies confined with it, " are suddenly introduced into the air, these " bodies will not suffer it to retain the whole, but, " as it may be said, it will be obliged to give up
" their

“ their quota to them ; and in that case the hy-
“ grometers, if there are any inclosed, will move
“ towards humid, although the air is not yet satis-
“ fied. A new portion of vapour will be shared in
“ the same manner, and so on continually, until
“ the perfect saturation of all the bodies ; at
“ length, if, after their saturation, vapours are still
“ introduced into this space, the superabundant
“ water will attach itself to their surfaces, will
“ wet them, and, although retained on these
“ surfaces by an adhesion which perhaps also be-
“ longs to chemical affinities, it may be wiped off,
“ or separated from these bodies by means purely
“ mechanical.

“ Now, let a new substance be introduced into
“ this space, more covetous of water than those
“ inclosed within it ; this substance will begin by
“ taking the superabundant water which wets the
“ surface of these bodies without being combined
“ with their elements : then, if this water is insuf-
“ ficient to saturate it, it will deprive those bodies
“ of it which are confined with it, until it has di-
“ minished its own drought, and increased their’s
“ to the point at which they become equal, and at
“ which there remains an equal tendency in all of
“ them to combine with water.

“ So if heat or any other cause augments the
“ tendency of some one of these bodies to unite
“ with water, without proportionally increasing
“ that of the other’s, it will also take away a por-
“ tion

"
tion of the water they contain, sufficient to bring
its attractive force to a level with theirs."

254. The passage I have just quoted offers, with much precision, facts very well calculated to show the laws followed by chemical action, and it may be observed that Saussure experiences some embarrassment in defining the difference between physical and chemical affinity : he gives way to an established opinion, or rather to an illusion which seems to point out another species of action ; but this distinction causes this learned observer to fall into a contradiction, for he declares, more than once, that the union of the vapour with air is owing to chemical affinity, and in this passage, he compares it to chemical solutions.

I cannot better point out the difference which chemists have made between the affinity which produces combinations, and that described by Saussure, and which has been adopted by philosophers in the explanation of several phenomena, than by citing the definition of the first by Guyton, who has treated so ably of all the properties which are attributed to it. " This attraction (chemical) is " elective, as Bergman has stated, that is to say, " that, of two substances presented to a third, it " drives off one and leaves the other; that a third " substance exercises an action on one of two sub- " stances which were originally united, which dis- " places the other."*

* Encyclop. Méthod. at the word *Affinité*.

Nevertheless when I consult the opinions formed with respect to the mutual action of bodies, by those who have studied natural phenomena in their greatest latitude I find that they have indicated one common origin to all its effects.

Monge, in discussing two hypotheses calculated to explain the formation of water, finds that one seems to require, *that by augmenting the dose of the solvent, its adherence for its basis is diminished; which is absolutely the reverse of what is observed in every analogous operation of chemistry.** It must be observed that by solution, he here means chemical combination, so that he considers that the force which produces it is modified by the quantity, as is admitted in physical phenomena.

Laplace, after having described the method of estimating the action of the different acids on ice, according to the temperature, adds: *If, in the same manner, we consider all the other solutions, we may measure the forces of the affinity of bodies for each other with precision; but this theory cannot be developed in a small compass, and we shall make it the subject of a particular Memoir.* He therefore included the quantity of an acid in the estimation of the affinities, for example, its energy and the variable resistance of the cohesion, as he had done with respect to the action of acids on ice: it is much to be regretted that he has not fulfilled his promise.

* Mém. de l'Acad. 1783. p. 83.

Newton, who slightly noticed the phenomena with which chemistry is occupied, in the explanations which he gave of them, has described the laws of the attraction which produces them, in the manner in which he comprehended them, by reasoning from general phenomena to particular facts; and if he is wrong in some applications, because the circumstances of the phenomena, and the elementary parts of the combinations which produce them, had not been determined with sufficient accuracy at the time in which he made them, it will nevertheless be found that his explanations are also reconcileable to the best elucidated facts.

He says,* "is not the deliquescence of salt of tartar produced by an attraction between the saline particles, and the aqueous vapours of the atmosphere? Why do not common salt, salt-petre, and vitriol, become also deliquescent, if not for want of a similar attraction? And why does salt of tartar only attract a certain quantity of water, if not, because as soon as it is saturated, it has no more attractive force? What other principle but this force prevents the water (which alone evaporates by a slight heat) from detaching itself from salt of tartar except by means of a violent heat?

" Is it not this same attractive force which is exerted between the moleculeæ of the vitriolic acid and the globules of the water, which is the cause why this acid attracts the humidity of the

* Opt. tom. II.

" air

“ air to saturation, and does not afterwards restore
“ it without much trouble, when it is submitted
“ to distillation ? ”

Newton also explains the production of other chemical combinations, without making any distinction in the laws which the attraction follows in these different circumstances: he saw in it only one property, which is more or less energetic, and which is weakened in proportion as saturation is established: saturation is the term at which it ceases to produce effects.

He remarks that in proportion to the strength of the attraction, a greater quantity of acid is required to dissolve a metal; so that, according to his opinion, the quantity of acid necessary to produce saturation is proportional to the force of affinity.

He attributes to the condensation which results from the combination, the solidity and degree of fixity which it acquires: for example, when muriate of ammonia is formed from muriatic acid and ammonia, both of them much more volatile, “ the united particles of these spirits become less volatile, because they are larger and more freed from water.”

He derives the properties of a combination from those which must belong to the elements composing it, in the conditions in which they are found: thus, in explaining the formation of muriate of antimony by oxigenated muriate of mer-

cury, he adds, "when the heat is stronger, the spirit of salt carries off the metal in the form of "a fusible salt, called butter of antimony, al- "though the spirit of salt is nearly as volatile as "water, and the antimony is nearly as fixed as "lead." It was this luminous principle, that the properties of a combination are dependent on those of the elements, laying aside the modifications arising from the reciprocal action, which enabled him to foresee that water must contain an inflammable substance.

255. The observations which I have collected in this first part seem to me to establish as a general fact, that the affinity belonging to each substance acts in the ratio of the quantity within the sphere of activity, conformably with the opinions which I have detailed : it results from this, that the quantity may make up for the force of the affinity, which excludes the elective affinities which unite two substances, whatsoever may be the opposition of the affinities which are considered as weaker, and independently of the quantities.

An immediate consequence of this principle is, that the saturation which any substance produces in those with which it can combine, is the measure of its peculiar affinity, as was thought by Newton ; hence I have sought the measure of the affinity of the different acids with the alkalis, in their capacity for saturation.

It

It was necessary to explain the facts that had led to the admission of an affinity capable of determining the choice of the substances which combine, and the proportions of the combinations which they form.

This explanation I have sought in the action of caloric, and in the reciprocal affinity of the moleculæ of a simple substance, or of the integrant parts of a combination, by making these causes concur with the affinity, in the formation of combinations, and in the explanation of chemical phenomena: I have consequently been obliged to give great attention to the effects of expansion and condensation on the constitution of substances, and on that which they acquire in the different circumstances.

The effects of caloric are different, not only according to the dispositions of the bodies on which it acts, but also according to the state in which it is itself found; it was therefore necessary to examine the difference of its action when its communication is immediate, or when it forms radiant caloric, and the correspondence which it has with that of light, and of electricity. The properties which bodies acquire by combination with caloric, are sometimes favourable to the action of affinity, and sometimes are adverse to it: I have considered them as forces which are obedient to regular laws, and whose effects must be appreciated according to the circumstances.

I have endeavoured to separate the effects of the immediate action of the affinity, which, in a greater or less degree, saturates those tendencies to combination which form the distinctive properties of substances, from those of the condensation which is a consequence of it: the one tends to unite all the substances which exercise a chemical action; the other frequently becomes an obstacle to this effect by the resistance which it opposes, or by the separations which it occasions, and thus, it may be said to distribute the saturation, to which it does not itself contribute.

I have employed the condensation produced by the reciprocal action of substances to explain the limits within which the proportions of the elements are circumscribed in some combinations: when the greatest effect of the reciprocal action takes place in certain proportions, these combinations must separate with a determinate composition, or else they acquire a peculiar existence, by opposing a resistance equal to the effort which produced the condensation, and which must be overcome by an increase of force to enable the progress of the chemical action to continue, unless the natural dispositions of the elements of a combination cause a variation in the result.

The force of cohesion which constitutes the solid state is an effect of the reciprocal affinity of the moleculæ, or of the integrant parts, which becomes more powerful than the expansive action of

of caloric: this predominance may be owing to the condensation produced by the combination: it becomes a still greater resistance to the action of the other affinities, not only because it results from a strong reciprocal action, but also because it obliges the other substances to be in a small quantity within the sphere of activity, and then the effect of a larger proportion is prevented.

Thus, the reciprocal affinity of two substances often tends to produce a saturation of properties: one effect of this action is a condensation which expels or compresses the caloric; from this condensation follows an augmentation of the reciprocal affinity of the moleculæ of a substance, or of the integrant parts of a combination: by this the reciprocal affinity causes a gazeous substance to pass into a liquid or a solid state.

The affinity which produces combination acts in the ratio of its quantity; but it can be saturated: the reciprocal affinity of the moleculæ, weak at first, almost null in gazeous substances, and independent of the quantities, increases by the combination in the ratio of the condensation, to which it may afterwards itself contribute more and more; it is compounded of those of the elements of the combination as well as the specific gravity: both affinities produce effects which are complicated with those of caloric, and which it is equally necessary to distinguish in physical phenomena

phenomena as in those which are considered as chemical.

Finally, I have endeavoured to demonstrate the share which substances, whose effects are usually neglected, may have in chemical action, by considering them simply as solvents, and the propagation of chemical action, more or less slow, which is analogous to the conducting faculty of heat.

I have been led by these different considerations to conclude that chemical affinity does not follow particular laws, but that all the phenomena which depend upon the mutual action of bodies are the effect of the same properties, of which chemistry seeks to embrace all the results; that, in this respect, no distinction is required between natural philosophy and this science; and, that the affinity of different substances which produces their combinations is not elective, but that it is variable, according to the quantities which act, and according to the circumstances which contribute to its effects.

Hence it follows, that the chemical qualities of different substances depend: 1st. on their tendencies to combination, which are mutually saturated, and which remain more or less predominant in the compounds: 2d. on their relations with caloric which produces their greater or less disposition to expansion, and which modifies the faculty for combination, by occasioning a variation in the quantity

quantity within the sphere of activity, and, by opposing elasticity to the condensation, which is an effect of the combination; 3d. on the reciprocal action of their moleculeæ which is added to the effect of the affinity which has produced a combination, but which is in opposition to their reciprocal action with other substances: 4th. on the relations to such other substances as in combining with them do not produce a reciprocal saturation of properties, but make a variable division and distribution of them, and principally of those which depend on the constitution. Whence it follows, that, in a compound, the origin of the properties which distinguish it may be discovered, by considering the saturation of its elements, and the condensation which they have experienced.

256. I have deviated from the general course of chemists: they have deduced the laws of affinity from the phenomena in which chemical action appears strong; I, on the contrary, have been desirous of tracing it from the commencement of its sensible effects to its greatest energy, by noticing the causes capable of modifying it; and, in my opinion, it is principally in its first effects, that its character can be particularly distinguished, because even its action generates affections in substances which become new forces and disguise its motions: thus, in a combination accompanied by a strong contraction, we are tempted to consider the fixed proportions which are determined by this

this circumstance as an attribute of the affinity; but, if the affinity is followed, either when the proportions are very unequal, or when it produces but a slight contraction, it will be seen that the action is proportional to the quantities which exercise it.

In undertaking a new investigation of all the powers which contribute to the results of chemical action, and on which the general theory of chemistry must be established, I do not flatter myself with having assigned its true limits to each, and still less with having indicated all the causes which can contribute to the facts on which I have relied: I have shown in the introduction what is my opinion of a general theory. Herein I have sought to establish a discussion of the principles to which, as it appears to me, too much latitude has been given.

In every discussion whose object is to ascertain the causes of phenomena, it must not be overlooked that it frequently happens that one or several analogous phenomena are equally explicable by two hypotheses, and that then two opinions, sometimes contradictory, may be maintained, until some modification of the effects is obtained, which, at length, excludes one of the two hypotheses: this is a circumstance in which opposite opinions can be supported even by experiment, and it will be difficult to prevent the natural interest we attach to our conceptions from engaging us to multiply

tiply that species of facts which is capable of receiving one of the two interpretations: nevertheless the philosophical spirit which throws such a radiance around chemistry in particular, will ere long dissipate the want of certainty which may divide our opinions: in the annals of the human mind it will be difficult to find a period more honourable to it than that which established unanimity so quickly on a theory which had predominated like that of phlogiston.

Having succeeded in distinguishing the general causes of chemical phenomena, it is still easy to be deceived in many applications of them, either because the circumstances which influence the facts are not sufficiently known, or because among the several causes which may contribute to them, that is attributed to some which depends on others.

It is this concurrence of several causes to the same effect that principally occasions the apparent anomalies, which sometimes lead to doubtful explanations, or which even render them impossible: in that case, without suffering these facts to invalidate the consequences drawn from more positive facts, we must suspend the explanation, or stop at conjecture.

I am aware that in the execution of the design to which I was led by the sudden establishment of the normal schools, and by the desire I have to review the hasty occupations in which it engaged me,

394 CONCLUSION OF THE FIRST PART.

me, that they may serve me as a guide in the instruction of the polytechnic school, a much more extensive acquaintance with the inquiries which have been greatly multiplied for some time was requisite: led away for several years by engagements foreign to science, since having been permitted to resume my studies, I have only been able to accomplish imperfectly the investigations of which I stood in need.

NOTES

NOTES

TO THE
FIRST VOLUME.

NOTE I.

FROM the degree of solubility of the combinations which can be formed, we may be able to judge of the salts which can be found together in a liquid, for example, in a mineral water, by admitting, for the conveniency of language, that these combinations enjoy an insulated existence in the liquid: thus, a water cannot contain carbonate of soda and a salt with a calcareous base at the same time. It cannot hold a salt with base of lime in solution with a sulphate, in a greater proportion than what could have produced the quantity of sulphate of lime which could have been held in solution, allowing, however, a little latitude for the augmentation of solubility which may be produced by the mutual action of the salts.

The difference of solubility at different degrees of temperature is the cause of a phenomenon which was first observed by Scheele, and afterwards by Green: * a water

* Journ des Mines. No. XXVI.

which

which contains soda, magnesia, sulphuric acid, and muriatic acid, yields muriate of soda during the evaporation, and sulphate of magnesia by cooling; but if the water is exposed to congelation, it is, on the contrary, sulphate of soda which crystallizes.

The solubility of the sulphate of soda diminishes so rapidly by the reduction of the temperature; that, according to the observation of Blagden,* this salt can only lower the freezing point of water one degree of Fahrenheit's thermometer, and then it separates and crystallizes quickly, while that of the muriate of soda diminishes very little; and this salt can lower the temperature 28 degrees of the same thermometer below congelation without precipitating, when its proportion is one part to four of water. A temperature a little lower than that of congelation will, therefore, produce the crystallization of the sulphate of soda, and the heat of ebullition, which greatly augments the comparative solubility of the sulphate of soda, occasions that of the muriate of soda. This difference, produced by the temperature, is therefore a natural consequence of the cause of the separation of salts by crystallization, and shows, in a convincing manner, that we must not consider the salts as ready formed in a liquid from which they can be obtained, since, by changing the relations of the solubility, the combinations which form are made to alternate, but that it is their difference of solubility in the circumstances in which they are found, that produces their separation and successive crystallization.

Green, who, with other chemists, considers the salts in a liquid such as they are produced by evaporation, says, that as soon as the sulphate of soda is separated by cold, it does not any longer yield muriate of soda when it is mixed with muriate of magnesia and submitted to evaporation, and that he has made several fruitless attempts on

* Philos. Trans. 1788.

this

this subject: I know not what can have deceived him, but having mixed equal weights of muriate of magnesia and dried sulphate of soda, and having evaporated the solution, a thick crust of muriate of soda was formed: the mutual action of the salts only augments the solubility of the muriate of soda to a certain point.

Although the sulphate of soda is very soluble in water, it nevertheless retains the water very feebly in its crystals, as is proved by the facility with which it effloresces in the air: by this I explain a fact which, at the first glance, seems to deviate from the rule I have laid down on the formation of salts, in the ratio of their solubility; when the waters of the salt-springs of La Meurthe are evaporated, an abundant deposit of sulphate of soda, deprived of its water of crystallization, is formed; nevertheless, a part of the sulphate of soda remains in the mother-water, and does not crystallize by cooling: the same thing happens in this case as when a dried muriate or nitrate of lime is mixed with a saturated solution of nitrate of pot-ash; a part of the nitrate of pot-ash is precipitated, because the salt with base of lime at first abstracts part of the water, although, by its action, it has the property of augmenting the solubility of nitrate of pot-ash.

A similar result is also obtained when a mixture of sulphate of ammonia and muriate of soda is evaporated; a considerable precipitate of sulphate of soda deprived of water is formed, although this salt has a solubility nearly equal to that of muriate of ammonia.

Davy has made some interesting observations * on the quantities of water which the nitrate of ammonia retains in its crystallization according to the temperature at which the evaporation is effected, and on the changes which this circumstance produces in its crystallization. The two

* Bibl. Brit. No. CXLVIII.

extremes seem to be the prismatic nitrate obtained at the temperature of the atmosphere, and which contains the most water of crystallization, and the compact nitrate, in very fine needles, which results from its evaporation at 119° Reaum. : the fibrous nitrate whose evaporation was made at 17° Reaum. holds a medium between these species.

It may happen that the insolubility of a salt is so governed by the action of one of the substances which is present that its effect is destroyed, and another order of combination is produced, to which a knowledge of the solubilities of the substances, when separate, did not lead; thus, when a solution of oxide of lead by soda is mixed with a liquid sulphate of soda, only a small precipitate is formed.* The greatest part of the oxide of lead remains in solution, although the sulphate of lead is insoluble and strongly resists the action of acids; but it is very soluble in the soda with which it is then in contact, and forms a triple salt with it, as magnesia does with ammonia and muriatic acid.

The effects which I attribute to the force of cohesion are in reality only due to the insolubility, that is to say, to the relation of the force of cohesion with the chemical action of the water; hence it arises, that the combinations determined by this cause are often very different, when the liquidity is produced by the sole action of the heat.

If a mixture of muriate of lime and sulphate of barites is urged by fire in a platina crucible, it enters into a fusion so liquid that it has the appearance of water; after being cooled, the mass is found to consist of muriate of barites and sulphate of lime, great part of which may be separated by a speedy washing, for if a continued ebullition was employed, the sulphate of lime would be decom-

* De l'Influence des Prop. Mém. de l'Instit. tom. III.

posed:

posed : for this curious experiment, which I have repeated, we are indebted, as I am informed, to the works which are executed in the laboratory of Seguin.

When in a similar manner a mixture of sulphate of soda and carbonate of lime is submitted to the action of heat, it enters into a very liquid fusion, and by the action which its elements then exercise, the sulphate, changed into a sulphuret by means of a mixture of charcoal, is converted into a carbonate in the process for obtaining a soda capable of replacing that of commerce, for which we are indebted to Citizen Leblanc.

These observations prove, that the force of cohesion which, when water is the solvent, produces the most energetic effects, can produce contrary ones when the same substances exercise a mutual action without the aid of water : they also prove, that the separations which take place are not the immediate effect of the comparative affinity, but of the force of cohesion, which becomes greater in some substances than in others in the existing circumstances.

It is true, that chemists have distinguished the affinities which are exercised *in the humid way* and those exercised *in the dry way*, but without pointing out the causes which produce a variation in the effects of a force which they considered as constant; and they blended those arising from a different state of liquefaction, and from the volatility occasioned by the action of heat. In one of the intelligent notes which Fischer has added to a German translation of my Researches into the Laws of Affinity, he observes, that Hahnemann had announced before me, in a translation of the Chemical Arts of De Machy, that the decompositions of chemical combinations depended, only on their relative solubility.

NOTE II.

(By FISCHER.)

THE subject of which Berthollet has treated at the end of the first part of his work on the affinities, had been spoken of in 1792 by Richter, in his Stechiometry, s. 1. p. 124. Guyton also mentions it in the Memoirs of the Institute for the year 1797, without being acquainted with Richter's work, which, though filled with very interesting experiments and observations, is but little known in Germany. But this is the author's fault, who should separate them from hypotheses, and not mix them continually with calculations which render them obscure to the generality of readers.

Richter expresses himself thus:

" If two neutral solutions are mixed together, and a decomposition follows, the products which will result will be, nearly without an exception, also in a neutral state. But if the two solutions, or one of the two was not neutral, neither will the products be so."

Richter has not given the exceptions, but Berthollet mentions some which take place when there are metallic salts in the mixture; perhaps there are not any other exceptions. The idea of neutrality does not seem applicable to these salts; they all preserve an excess of acid in the liquid state; their bases are not soluble in water, and they do not act on the acids like alkalis. These are, nevertheless, the conditions necessary to neutrality. Although this is the case, we may, with Richter, Guyton, and Berthollet, consider the law as established, when an alkaline base and an acid are in question.

From this the following conclusions may be drawn:

1st. The quantities of two alkaline bases necessary to neutralize

neutralize equal parts of an acid, are in proportion to the quantities of the same bases necessary to neutralize every other acid.

Let A and B be two acids, a and b two alkaline bases. The two neutral salts Aa and Bb, are supposed to be such that they change bases completely by their mixture. It will then result from this supposition, that A neutralized at first by a, will be so afterwards by b, and that consequently the quantities of a and of b which are capable of neutralizing A, will be capable of neutralizing another quantity of B which is fixed.

It is clear that the words *bases* and *acids* may be changed, and that the law is applicable to all neutral combinations, even though Aa and Bb do not change bases, since the experiment can always be reversed by mixing Ab with Ba.

2d. If Aa, Ab, Bb are known by experiment, Ba can be found by calculation. Richter has employed this conclusion to find the proportion of neutralization, though it is difficult to fix it immediately; but he has, in a great measure, determined the proportions by experiment.

3d. When it has been found by experiment how much alkali or earth is required to neutralize 1.000 parts of sulphuric, nitric, or muriatic acid, it will be obvious that each table contains other numbers; but the numbers of each table will, with respect to each other, be in the same proportion as the numbers of the other give them. The same thing will take place if we examine how much acid is wanted to neutralize 1.000 parts of soda, ammonia, or lime.

It is in this view that Richter has treated the matter. He has taken the trouble to examine each acid, in its relation to the bases, by experiment and calculation, and to give his results in tables; this has filled the greatest part of his works from 1791 to 1800.

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It appears that Richter was not aware that all his tables may be reduced into a single one of 21 numbers, divided into two columns, by means of which they may be all reduced by the rule of three. The following is that which I have calculated from Richter's new tables, several of which differ from the former ones, (see Numbers 8 and 10 of his ideas on the new subjects of chemistry).

BASES.		ACIDS.	
Alumine	525	Fluoric	427
Magnesia	615	Carbonic	577
Ammonia	672	Sebacic	706
Lime	793	Muriatic	712
Soda	859	Oxalic	755
Strontian	1329	Phosphoric	979
Pot-ash	1605	Formic	988
Barites	2222	Sulphuric	1000
		Succinic	1209
		Nitric	1405
		Acetic	1480
		Citric	1683
		Tartareous	1694

The intention of this table is, that if an article in one of these two columns is taken, for example, pot-ash in the first, to which the number 1605 corresponds, the numbers of the other column will show how much of each acid is required to neutralize these 1605 parts of pot-ash : they will require, for example, 427 parts of fluoric acid; 577 of carbonic acid; &c. If an article of the second column is taken, the first is to be used to know how much earth or alkali will neutralize it.

It may be said, that all these numbers are to be considered as representing the force of affinity, and the articles of one column which are near to each other are in the inverse

verse proportion of the two numbers of the other column which correspond to them, (See Berthollet, Art. X., and XV.). Pot-ash and soda are in the proportion of 859 to 1605 for each acid; but it follows from Berthollet's inquiries, that the numbers are not sufficient to explain the phenomena of simple and double affinity by calculation.

It is obvious that Richter's work contains excellent observations for the theory of affinities; but it also contains many unfounded hypotheses, among which I rank what he says on the bulk of masses.

Richter gives a determinate order to his tables according to the amount of the numbers; but he makes subdivisions of each column, placing the three alkalis separately on the side of the bases, as well as the fluoric, sulphuric, muriatic, and nitric acids, on the side of the acids. In the end, he is of opinion that another law must exist in the manner in which the numbers follow, and, after long calculations, he finds that the numbers on the side of the bases should be considered as making part of an arithmetical progression, and those on the side of the acids as making part of a geometrical progression.*

It is certain that the numbers of the tables may be considered as series in progression; but Richter is wrong if he believes he has found in them the law of the proportions of neutrality, or of the forces of affinity. It is a property of all numbers to be capable of being considered as making part of an arithmetical or geometric

* The series of three alkalis is represented by a , $a+b$, $a+5b$; the series of the earths by a , $a+b$, $a+3b$, $a+9b$, $a+19b$. The series of the four mineral acids is represented by c , cd^3 , cd^5 , cd^7 ; and the series of the other acids (the phosphoric acid excepted) by c , cd^3 , cd^4 , cd^8 , cd^{11} , cd^{14} , cd^{15} , cd^{16} .

series.* Richter may do the same thing without his subdivisions, as I have done in the table which I give. It is still more easy, if the liberty of increasing or diminishing a number is taken, as Richter does occasionally.

NOTE III.

Wendwoot makes two objections to the use of the calorimeter, which are the more deserving of being examined as they prevented him from using it to determine the quantities of caloric which are represented by the degrees of his thermometer; which would have established an exact comparison between the degrees of this thermometer, and would have given it an advantage of which even the mercurial thermometers are deprived.

The first of these objections is founded on the property which ice has of absorbing a certain quantity of water, which in his opinion renders the results uncertain: he did not observe that when the ice is below zero the authors have directed that *it is to be bruised, to be spread in very thin layers, and to be kept so during some time in a place whose temperature is above zero.* They add, it must be seen that, at the beginning of each experiment, the ice has already imbibed as much water as it can retain in that manner.

It is evident that with these precautions the water which the ice absorbs cannot be a cause of error, since it

* If we take the logarithms of a series of numbers, we shall see that they may be considered as making part of an arithmetical series: the numbers of the series will then make part of a geometrical series.

† Philes. Trans. 1784.

is, in this respect, in the same state before the experiment as when it is finished.

Wedgwood's second objection is founded on the property of water, just liquefied, of resuming the state of ice at the same temperature: on this subject he has made some curious experiments, which prove that the contact of solid bodies is really capable of producing a new congelation in water which has just liquefied, and that they differ from each other in the degree of this property: he explains this phenomenon principally by an evaporation which he supposes is produced by the cold.

Its true cause appears to me to be the attraction exercised by the solid, and by which it would have been wetted, if the water had been farther from the term of congelation; but in the state in which it is, this action is enabled to overcome the remaining power of caloric to produce liquidity. It is therefore a phenomenon analogous to the separation of a salt in solution, by a crystal of the same salt, or even by any other solid body, or to the congelation of water which is determined by the contact of ice, (27); but this cause cannot produce any sensible error in the experiments made with the calorimeter, and a strong proof that it is not subject to the uncertainties supposed by Wedgwood, is, that the same experiments many times repeated have given results whose differences were very trifling, and such as exist in those physical experiments which are considered as the most exact.

NOTE IV.

THE changes of temperature produced in air which experiences a dilatation or a condensation, and which abandons or takes caloric, according to the dimensions given to

to it, have received different explanations ; but they have always been supposed to be conformable to the indications of the thermometer : Cullen, who appears to be the first that noticed the descent of the thermometer by the dilatation of the air in an air-pump, attributed it to cold produced by an evaporation ; but Saussure proves that air dried by an alkali lowers the thermometer nearly as much as humid air, when it is dilated in an air-pump ; that the hygrometer remains immoveable at the greatest drought ; and that consequently evaporation could not be the cause of the cold produced.* Lambert observed that the cold was more considerable the more quickly the air was rarefied, and he explained it by particles of fire carried away by the air, and replaced gradually by other particles emanating from the receiver : this idea, which is a little vague, has been adopted by Saussure.

Nevertheless this celebrated philosopher is obliged to make other suppositions to explain other facts which are naturally derived from the cause which I have indicated : Nollet was of opinion, that when the air was withdrawn from the driest receiver, a vapour or cloud was always formed which appeared to fall or be condensed at the end of a few seconds ; Saussure has shown that this appearance did not take place when the necessary precautions were employed to have a perfect desiccation, so that the formation of this cloud requires that the air should have a certain degree of humidity, or that some part of the apparatus should contain humidity : he believes that in Nollet's experiments *there was a concealed humidity in the tubes of his pump, which, changing into elastic vapours when the air was rarefied, rushed with force into the interior of the receiver.*

He is of opinion that the vesicular vapours form at a

* Essais sur l'Hygrométrie.

distance from the hair of the hygrometer which is not affected by them, and moves towards dry; this is contrary to observation, for when the air is saturated with water in a suitable degree, the vesicular vapours and their brilliant colours are instantly perceptible through the whole extent of the receiver: the dilatation occasions the reduction of the water from the hair into vapours, it must therefore move towards dry; but when the quantity of water held in solution is sufficient, the cold which supervenes causes a part to be reduced into vesicular vapour, because its intensity, at this moment, is such, that its effect with respect to the vapour is superior to that of the dilatation; the part precipitated by the cold is quickly redissolved by means of the communicated temperature, so that the bubbles disappear: if after having compressed the air the pressure is removed, the cold produced by its dilatation also gives rise to the vesicular vapour; but when the air is compressed the vesicular vapours are not perceived, although the hygrometer moves towards moist, because the temperature of the air is then too much elevated, and the moisture will be deposited on the sides of the apparatus by the reduction of temperature which succeeds.

Pictet * states some facts which led him to suppose that the fire, in the motion which is peculiar to it, carries away the water from a hygrometric hair or restores it to it, according to the direction of its motion; he consequently borrows from Deluc the qualification of *differential fluid*, which he gives to the fire, to which he has attributed this conveyance of the vapour.

This supposition appears to me incompatible with the idea which should be formed of caloric, either combined with a substance, or radiant, and with what we can con-

* Essais de Phys. p. 145.

ceive of the mechanical force of fire which moves in an horizontal direction, so that if the facts were inexplicable, that would be no reason for admitting it. The facts are as follows :

Having placed a thermometer and a hygrometer in a globe exhausted of air, but filled with aqueous vapours at a temperature of 4° , he removed the globe into a neighbouring chamber, the temperature of which was precisely at the term of congelation : the hygrometer which indicated 98° moved towards dry, and at the end of 4 minutes marked no more than 91° ; the thermometer in the globe was cooled one degree ; the hygrometer continued to descend towards dry, and some minutes after it was no more than 89 ; but at the expiration of 20 minutes, the thermometer in the globe having arrived at 0° , the hygrometer was found to have re-ascended to 94° , and 5 minutes later it was at $91\frac{1}{2}^{\circ}$, where it remained stationary. The globe had scarcely remained a minute in the lower temperature when a dew appeared. Having removed the globe from a lower temperature to a higher one, the same phenomena took place in an inverse order.

While the part of a vapour which first receives a reduction of temperature is reduced into a liquid, that which remains in the state of vapour will maintain nearly the same temperature, as takes place with the water in which ice is formed, because the part which becomes solid supports it, by the caloric which it abandons ; the hair is therefore in a rarer vapour, but in a temperature which is similar, or very little different, it will therefore move towards dry until the temperature is reduced, and brought into equilibrium with the surrounding bodies ; then the hair has attained that hygrometric state which is suitable to the humidity and to the temperature : in the contrary case, the evaporation had an equal influence on the temperature, and consequently on the hygrometric state.

This

This explanation is confirmed by the thermometer itself following the same motion, and it is probable that it does not indicate the state of the temperature correctly, on account of the radiant caloric which it may receive from, or yield to the globe.

NOTE V.

" It has been long known, that at the same temperature, the elasticity of a similar quantity of air, is very nearly reciprocal to its volume. This property is common to all the gases, and also to all the fluids in the state of vapour. It results from this, that, at equal temperatures, two moleculeæ of air, more or less distant, will always repel each other with the same force; so that if their repulsive force is represented by the action of a spring extended amongst them, the tension of this spring is the same whatsoever may be their natural distance. Let us, in fact, conceive a mass of gas or vapours, inclosed in a bladder which communicates with a bent tube, partly filled with mercury, and let us suppose that its spring raises a column of mercury of 75 centimeters in height; let us now conceive, that by compressing the bladder, the gas is reduced to half its volume, it is obvious that, in this new state, the stratum of the gas contiguous to the surface of the mercury will have a density twice as great as in its first state, and that consequently there will be twice as many springs pressing on this surface: thus, since in conformity with experience the height of the column of mercury becomes double, it follows that the tension of these springs must be the same; this tension, therefore, is not changed by the approximation of the mole-

culæ

“ cule of a gas, it only multiplies the number of the
“ springs applied to the same surface.

“ Hence, it follows that the molecules of a gas are
“ only sensibly obedient to the repulsive force of heat,
“ and that their action of affinity on each other is very
“ small in comparison with this force. Thus, their spring
“ depends only on the temperature; and the quantity of
“ free heat which exists in a mass of gas or of vapours is,
“ at an equal temperature, proportional to its volume;
“ for if, in the same volume, there was a greater quan-
“ tity in the state of condensation than in that of dilata-
“ tion, the repulsive force of two neighbouring molecule
“ would be augmented by it.

“ In diminishing, therefore, the volume of a gas, by
“ one third or a half, a third or a half of the free heat
“ existing in its molecules will be disengaged. If this
“ disengaged heat could be exactly measured, the quan-
“ tity of free heat contained in a given volume of the gas
“ could be determined; but this measure is very difficult
“ to obtain by means of the thermometer, either because
“ part of the disengaged heat spreads to the surrounding
“ bodies, or is developed in radiant heat, or because the
“ mass of the thermometer, however small it may be, is
“ very great with relation to that of the gas which is
“ condensed. Experiments made with the calorimeter
“ would give it in a very accurate manner. Heat thus
“ disengaged has a sensible effect on the velocity of
“ sound; it occasions an excess of this velocity above
“ that given by the ordinary theory, as I have satisfied
“ myself by calculation.

“ It follows therefore from what precedes, that if we
“ conceive equal volumes of two different gases enclosed
“ in two coverings of the same capacity, and inextensible;
“ if we suppose that at a given temperature the spring of
“ these two gases is the same, by increasing their tempe-
“ rature

“ rature in the same manner, the increase of their spring
“ will be the same, since it depends only on the tempe-
“ rature. Let us now conceive that the coverings which
“ contain them cease to be inextensible, the two gases
“ will dilate until their springs are equal to the pressure
“ of the atmosphere which encircles these coverings; and
“ as the volume of each gas is in the inverse ratio of its
“ spring, the two gases will take the same volume, and
“ will dilate equally. In fact, this has been ascertained
“ by Citizen Gay Lussac by a great number of experi-
“ ments. From what has been just said, it is obvious
“ that this interesting fact is coupled with that of the
“ increase of the spring of gases in the inverse ratio of
“ their volume; and, consequently, with this general
“ principle, that the repulsive force of the moleculæ of
“ gases is independent of their mutual distance, and de-
“ pends only on the temperature.”

NOTE VI.

COUNT RUMFORD has made a curious experiment on the heat produced by friction;* he caused a blunt piercer to move with rapidity in a cylinder of brass of 13 pounds, English weight, and observed that, in the space of two hours, and by a pressure equal to 100 cwt. the piercer had reduced 4115 grains of brass to powder, and that, during the operation, a quantity of heat was disengaged which would have raised 26.38 pounds of water from the temperature of congelation to that of ebullition, but he found no difference between the specific caloric of the metallic powder and that of the brass which had not expe-

* Essays, Vol. II.

rienced

rienced the friction, which induced him to believe that the heat is only owing to the motion communicated, and not to caloric, such as it is considered by the generality of chemists.

I shall confine myself to examining whether the result of this experiment obliges us to renounce the theory of caloric, considered as a substance which enters into combination with bodies, and whether a satisfactory explanation of it cannot be given by the laws deduced from the comparison of its other effects.

In considering the disengagement of caloric as an effect of the diminution of volume produced by the pressure, it is not the filings alone which would contribute to this disengagement, but also all the parts of the cylinder of brass, though in a very unequal manner, by the expansive effort of the part which experienced the greatest compression and the highest temperature, without being able to attain the dimensions suitable to that temperature, on the parts least heated and least dilated, so that there must have been a condensation of the metal in respect of its natural dimensions, which diminished from the place of the strongest compression to the surface, supposing the effect uniform through all the cylinder.

By the diminution of volume a heat would be disengaged equal to that which would have produced a similar augmentation of volume, admitting that the specific heat of the metal does not change in this extent of the thermometric scale, and that the dilatations are uniform, which will be but little different from the fact at near temperatures and dilatations. All the disengaged heat would have given nearly 160° of Reaumur's thermometer to the cylinder, and, if the dilatation of brass by heat is equal to that which has been found in iron, and which is $\frac{1}{500}$ for each degree of the thermometer, the 160° would have produced a dilatation of $\frac{1}{300}$ in each of its dimensions,

dimensions, and the reduction of volume owing to the pressure, supposed equal to this augmentation, must have produced the same degree of heat.

Now percussion, the action of a fly-wheel, the compression of a wire-drawing machine sometimes produce a considerable change in the specific gravity of metals; it appears, for example, that it is augmented more than a twentieth in platina and iron which are forged.

It is obvious, therefore, that Count Rumford's experiment is very far from reaching the limits of an explanation founded on a known and incontestable property.

It is easy to make imposing approximations on the phenomena of caloric, but if a person little habituated to chemical speculations was told that Count Rumford's cylinder, by a violent friction for two hours, gave as much heat as would have been absorbed by 15 kilogrammes of ice in its reduction into water, without change of temperature, or by two hectogrammes of oxygen gas in its combination with phosphorus, I am uncertain which of these phenomena would surprise him most.

The small changes which supervene in the quantity of combined caloric have so slight an influence on the capacity for caloric within a small extent of the thermometric scale that they become entirely inappreciable, and we have not yet the necessary data to ascertain what the changes are, in this respect, which take place in a solid body, according to the state of condensation to which it has been brought by a mechanical force and at remote temperatures.

Besides, in the experiment which Rumford made to examine the specific heat of the brass filings which he had formed, he heated them to the temperature of boiling water; but this very elastic mineral, as soon as it became free, and particularly in this latter operation, must have partly resumed the state of dilatation and proportion of caloric

caloric which are suitable to it at a certain temperature, and by that means the effect of the compression it had experienced must have disappeared in part, as a metal which has been hammered (ecroui) is observed to resume its properties by being nealed.

NOTE VII.

“ This, says Deluc,* is an experiment by which Watt convinced himself that water loses more caloric in proportion, by the ordinary evaporation than by ebullition. This experiment, which he was so obliging as to repeat in my presence, six or seven years ago, was made in a tin vessel, about eight inches in diameter, containing water warmer than the place, and submitted to evaporation in the open air: the vessel also contained a thermometer, which, on gently agitating the water, indicated exactly the losses of heat experienced by it, while at the same time the losses of weight were shown by a balance to which the vessel was suspended. Another vessel similar to the first, and containing the same quantity of water, at the same temperature, was placed at a small distance, but in this the water was covered with oiled paper to prevent its evaporation. After the experiment, the heat lost by the last vessel was deducted from the loss of heat sustained at the same time by the vessel in which the water evaporated, and the difference of this loss having been compared with that of the weight, the result was that the evaporated water, considered by itself, had taken from the vessel a quantity of fire proportionally greater than what is contained in the vapour of boiling water.”

* Ann. de Chim. tom. VIII. p. 79.

According

According to the principles which I have laid down, the water which, in evaporation, takes the elastic state by its combination with the air, will take a quantity of caloric proportionate to its real volume, and to the temperature on which its tension depends: now the vapour of water which is formed under the pressure of the atmosphere, and at a degree of heat equal to 80 degrees, must, from these two conditions, be superior to that held in solution by the air, under the same pressure and at a lower temperature.

It appears that it was from this experiment that Watt concluded that the specific caloric of the vapour of water was so much the less as the pressure under which it was formed was greater.

Was there not some circumstance which deceived him as to the true result? In the vessel which was uncovered, and the water of which had a temperature superior to that of the air, the part of the liquid which took the elastic state by combining with the air, communicated to it a specific lightness greater than if the air had been heated to the same degree without combining with the water, there must therefore have been a more rapid current established above the uncovered vessel than above the other, and a much greater quantity of air must have been heated and have contributed to cooling the first.

NOTE VIII.

Deluc is of opinion,* that of all liquids mercury is that whose changes of volume represents the variations of heat most accurately, even at very low temperatures: in support of this opinion he supposes, 1st. that the mer-

Recherch. sur les Mod. de l'Atm. tom. II.

cury does not experience any contraction by congealation; 2d. that alcohol dilates in congealing, and that this dilatation affects its movement by the reductions of the temperature, like that of water which approaches congelation; but Cavendish has shown that mercury experiences a contraction equivalent to the dilatation occasioned by its elevation to 404° Fahr.: in an experiment by Braun it seems to have exceeded even 500°, which gives a contraction of $\frac{1}{11}$ of its volume. The congealation of alcohol has never been effected by the greatest cold yet produced. Besides, nothing leads to a belief that it would experience an augmentation of volume if its congelation should be obtained. Analogy also gives us reason to think it must experience a contraction, since oils contract according to the observation of Deluc, and, according to that of Cavendish, nitric acid and sulphuric acid admit of the same effect; so that contraction, which is a consequence of the increase of the reciprocal action, seems to be the most general phenomenon, and the dilatation observed in alcohol, mixed with water, must only be attributed to the latter.

There is no reason to believe that the contraction experienced by a liquid which passes to the solid state does not produce an effect at the different degrees of temperature which precede that of their congelation, as the dilatation occasioned by crystallization produces an opposite one, and as is also the case with the dilatation arising from heat; for Deluc has shown that the nearer liquids approach to vaporisation, the greater are the dilatations they experience from the same degree of heat.

There are, therefore, two causes in liquids which prevent their condensation and dilatation from being the exact measure of their changes of temperature; the first is the progressive dilatation they experience in approaching vaporisation; the second is the dilatation or condensation

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sation to which they are subject in approaching congelation, and the effects of these two causes are complicated and varied according to the distance which separates them in each liquid.

The motion of mercury will be more regular at elevated degrees of temperature than that of alcohol, and that of oils, which, in this respect, are different according to their volatility. At inferior degrees, on the contrary, alcohol will show the differences of temperature with more accuracy, and it appears to me that the difference between its indication and that of the mercurial thermometer must not be considered as an irregularity belonging solely to the alcohol, for Deluc observed that a thermometer made with alcohol was only at $7^{\circ}7$ when that with mercury marked 10° , and Blagden having put two alcoholic thermometers with a mercurial one into a frigorific mixture, one of the two first marked 29° , and the other 30° , while that with the mercury was at 40° Fahr.* although these thermometers had been adjusted at the freezing point.

NOTE IX.

BECAUSE caloric is most generally disengaged in the form of light from that species of combination, which for that reason is called inflammation or combustion, we are led to consider every disengagement of light as the effect of combustion, or of a combination in which the oxygen experiences a condensation, and, if experiment shows combinations in which there is a disengagement of light

* History of the Congel. of Quick-silver. Philos. Trans. 1783.

without oxygen being concerned in it, to conclude that the theory adopted with respect to combustion is inconsistent. This opinion is supposed to be tenable from the experiments published by the Dutch chemists, whose association has produced investigations so important to chemistry, on an ignition which offers the appearances of inflammation, although it does not arise from the condensation of oxygen,* but from a combination of sulphur with the metals.

Scheels had before noticed the phenomenon which was the subject of the inquiries of the Dutch chemists : he says, † " it is observed in almost all the combinations " which the metals, that are susceptible of it, form with " sulphur, by fire, that the mixture inflames at the same " instant. An effect of the same kind takes place when " these mixtures are made in close vessels. I mixed three " ounces of iron filings with one ounce and a half of sul- " phur in fine powder, and put them into a small glass " retort which was three quarters filled : to its neck I " attached an empty wet bladder, and I placed the retort " gradually on burning coals. When the bottom of the " retort began to grow red, the edges of the mass burnt " with a beautiful purple-red light, which extended more " and more until the middle was also red : then the edges " grew dull, and at length the purple light disappeared " in the middle.....I distilled sulphur with filings of lead, " and obtained the same deep red light."

The Dutch chemists, who made similar experiments, observed that copper was the most proper metal to produce this phenomenon ; that the most suitable proportion was 40 grains of the metal and 15 grains of sulphur, and,

* Expér. sur l'Inflammation du mélange du soufre avec différents métaux. Journ. des Mines. No. II.

† Traité Chim. de l'Air et du Feu, p. 192.

that

that by diminishing or increasing the latter, the effect was weakened ; that after copper, came iron, lead, tin, and finally zinc ; but that antimony and bismuth did not offer this property.

I repeated the experiment with copper, and also on much more considerable proportions, and observed that the disengagement of the purple light was accompanied by a great heat, which, if suddenly produced, broke the glass vessel containing the mixture, and that this effect was instantaneous, and only lasted while the combination of the sulphur and the metal could be accomplished.

I was unable to produce this ignition with zinc, but the sulphur was entirely volatilized, and, in fact, sulphur does not enter into combination with zinc, which makes me believe that the Dutch chemists have confounded the true combustion of the zinc with the ignition in question, especially as they were obliged to employ the strong action of bellows, and as the flame, in this case, was vivid, clear, and white, which is the character of the combustion of zinc.

These experiments have been repeated at Turin,* where it was observed that when a sulphuret of iron formed by a slow fire was submitted to a heat sufficient to reduce the mixture into one mass, after the fulgoration, it had the appearance of a substance much more solid than before.

The authors of these experiments found that with the oxides and sulphur, sulphureous acid was formed without a disengagement of light, and that, on the contrary, the luminous appearance was obtained with the metals without the production of acid : from this they conclude that these facts "seem to confirm the doctrine of Stahl, and "to destroy, at least in part, that of the pneumatic chemists on the nature of metallic reguli."

* Mém. de l'Acad. de Turin. tom. VI.

It appears to me that facts should not have been selected to combat the doctrine called pneumatic, which are completely explained by its principles. The oxides can form the acid because they can yield oxygen to the sulphur; they do not give light during the act of their combination, because the volatile acid which is disengaged takes the caloric in combination.

NOTE X.

SEVERAL bodies become luminous in different circumstances; it appears to me that the causes of this phenomenon may be referred to the following:

A body becomes luminous either because its temperature is raised, or because it undergoes combustion, that is to say, a combination with oxygen, or because, when exposed to the rays of light, it absorbs a certain quantity which only enters into a feeble combination, and which preserves its elastic state, as it is seen that air is retained by the affinity of some bodies, by which it loses only part of its elastic state.

The light produced in bodies by friction may arise either from the temperature being raised by the compression and approximation of the particles which experience it, or from the combustion; these two causes may be found united. Thomas Wedgwood has proved that solid bodies became luminous when they attained a certain temperature which does not seem to differ much between them;* when therefore the compression can produce on some of the moleculæ, an approximation so great as to raise their temperature to a suitable degree, they will become lumi-

* Philos. Trans. 1792.

hous, although this difference of temperature can have but a weak influence on the thermometer and on neighbouring bodies.

The same chemist has made an interesting observation on this phenomenon, which is, that a body becomes luminous when its heat proceeds from a substance which does not possess this property, for instance, from a gas, the same as if it had been communicated to it by a luminous body, which confirms the substantial identity of light and caloric.

The light arising from the elevation of the temperature of bodies is produced when they are placed in azote gas and carbonic acid, as well as in oxigen gas: that, on the contrary, which is owing to combustion does not take place but in proportion to the oxigen which is present to produce it.

The luminous property of several substances, which have been confounded under the name of phosphori, belongs to this second species; such are Canton's phosphorus, the Bologna phosphorus, some nitrites, &c.

The property of these substances is augmented by raising their temperature, but their destruction is hastened by it.

Hulme has lately published some curious experiments on a light of this description which is emitted spontaneously by some fishes, and by other substances.*

The fishes which were principally the subjects of his experiments were mackarel and herrings.

The light which emanates from them precedes the putrefaction, which destroys it; it is produced equally by the internal parts, when they are exposed, and by the surface; it is fixed in a liquid which oozes at the surface,

* Philos. Trans. 1800.

and from which it may be separated by means of the blade of a knife.

This matter communicates its luminous property to some liquids, and not to others: water alone does not become luminous, nor does it when impregnated with the carbonic or other acids, with alkali, lime, sulphurated hidrogen, &c.; it becomes luminous when it holds the greater part of the neutral salts in solution; but it is requisite that the proportion of the salts be not too great, then the liquid acquires this property by a sufficient addition of water: agitation increases the effect. The surface is the most luminous; the light lasts for several days, after which it is at an end.

The appearances, which I have myself observed, have led me to believe that they depend on phosphorated hydrogen gas; but precise experiments are wanting to decide on the cause of this property.

Hulme also observed, that a glow-worm, placed in a very low temperature, ceased to be luminous; that it regained this property by being brought into a higher temperature; that old wood and other luminous substances are similarly affected by changes of temperature; that a heat which is near to that of the boiling point of water also destroys this property; that glow-worms retain it after their death, which proves that they do not receive this quality from respiration; the thermometer is not at all influenced by any of these luminous bodies, doubtless because the caloric is disengaged in the form of light.

Finally, certain bodies become luminous when they are exposed to a vivid light; they seem to experience no change in their composition, although this phenomenon is repeated often. In these, I admit a feeble combination of light which partly retains its elastic state; but it is only by analogy that I am led to this explanation; the cause

cause of this luminous property is much more obscure and uncertain than the preceding.

I have said, that the presence of oxigen was necessary to the disengagement of the light proceeding from a combination; nevertheless this cause must not be considered as the only one, as I have remarked in the preceding note.

NOTE XI.

I HAVE thought it important to determine the difference which exists between the action of the electric fluid and that of caloric, and the cause which frequently renders their effects similar, more especially as in the lessons of the Normal Schools this similitude of effect made me adopt the opinion of those who have considered the electric fluid to be caloric itself; I consequently requested permission of Citizen Charles to make use of his powerful apparatus in the experiments which appeared to me to be necessary on this subject. With that civility which those engaged in similar pursuits are always sure to experience from him, he undertook to perform them himself; I now give the result such as it was communicated to me by Gay Lussac, who assisted in the experiments.

A wire of platina was submitted to shocks which were nearly strong enough to effect its combustion, and to be satisfied of this a shock was excited by which a great part of the wire was melted or dispersed; afterwards the shocks employed were a little weaker, and immediately after each the wire was touched to judge of the temperature it had acquired; a heat was felt which was dissipated in a few minutes, and which, at the utmost, was estimated to resemble that of the boiling point of water. If electricity

city liquefied metals and brought them into combustion by the heat it excites, the platina wire must, after a shock which differed but little from that which would have produced its dispersion and its combustion, have approached the degree of temperature which occasions its liquefaction: now this degree, which is the most elevated that can be obtained, would, according to the valuation, more or less accurate, of Wedgwood, be 32277° of Fahr.

When the shock is sufficiently strong to destroy the aggregation of the platina wire, it begins by detaching moleculæ from its surface, which exhale like smoke; if it is strong enough to produce combustion, the remains of the wire appear to be torn into filaments.

A thermoscope, blackened with ink, and placed in the stream of a strong electric spark, only experienced a dilatation which was nearly equal to one degree of Reaumur's thermometer, and this slight effect might depend on the oxidation of the iron of the ink: placed beside the current, it did not show any dilatation, although the air was necessarily affected by the electric action: it was the same when it was placed in contact with a metallic conductor which received a stream less powerful than in the preceding experiments.

A cylinder of glass, filled with air, with an exciter at each of its extremities, to one of which was fixed a tube communicating with another cylinder filled with water, produced an impulse at each shock which raised the water more than a decimeter above its level; but its effect was instantaneous.

These experiments seem to me to prove, that electricity does not act on substances, and on their combinations, by an elevation of temperature, but by a dilatation which separates the moleculæ of bodies. The slight heat observed in the platina wire is only the effect of the compression

pression produced by the moleculæ which first experience the electric action, or which experience it in a greater degree; it must therefore be compared to that excited by percussion or compression.

If the dilatation was the effect of heat, that experienced by a gas in the experiment related above would not have been instantaneous, it would only have experienced a progressive diminution by cooling, as when its expansion is owing to heat.

In the experiment by which ammoniacal gas is decomposed, the gas indubitably receives the electric action, and nevertheless it is not heated, and as soon as the decomposition is finished, its volume remains unchanged, because the electric action which is employed in this experiment is not sufficiently energetic to cause a perceptible dilatation. No sensible dilatation is produced in a gas by a shock which is not very strong, because the impulse not being gradual, like the expansion arising from caloric, and being excited instantaneously, the resistance of the liquid becomes too great, and cannot be overcome unless the dilatation has great energy.

An experiment of Dieman and his learned associates confirms this explanation; they caused a shock to pass through lead placed in a vessel filled with azote gas which could not oxidate it; it was reduced into powder retaining all its metallic properties: if it had experienced a similar liquefaction by the action of heat, it would have cooled gradually, and would have congealed into one, or at least into several masses.

When a metal is submitted to the electric action, the effects produced immediately by the electricity must be distinguished from those which are owing to its oxidation: the first are limited to the diminution or destruction of the effects of the force of cohesion; to removing and dispersing the moleculæ: if by this a little heat is disengaged,

gaged, it is only owing to the compression sustained by some of the parts; but those which are occasioned by the oxidation produce a high degree of heat, and then the effects assume all the appearance of an ordinary combustion; hence it arises that the most oxidable metals are those which become red with the greatest facility, and which most show the properties of a metal liquefied by heat.

Electricity favours this oxidation inasmuch as it diminishes the force of cohesion; it is thus that an alkali renders the action of sulphur on oxygen much more powerful, by destroying the force of cohesion opposed to it, and that a metal dissolved in an amalgam is oxidized much more easily than when it is in a solid state. It is only by destroying the effects of the force of cohesion that heat itself produces the oxidation of metals, but the expansive action of electricity will have a great advantage over that of caloric, because its action is confined to the solid which it encounters in its course, so that the gas itself will not experience a dilatation in opposition to the condensation which accompanies the combination: to this circumstance may be applied what is observed on the action of hydrogen gas, which is capable of completely reducing an oxide of iron placed in the focus of a burning-glass, although water, whose two elements receive the heat equally, is decomposed by this metal.

It is probable that it is also to the expansive effect of an electric current established between two metals, having a stratum of water interposed, that the oxidation observed by Fabroni between these substances, placed in contact in water, is owing, and which, in this case, appears to be confined to the combination of the oxygen which is held in solution in this liquid.*

* Journ. de Phys. Vendém. An. X.

All the chemical effects produced in substances submitted to the action of electricity seem capable of being deduced from these considerations, and of being explained by the diminution of the force of cohesion which is an obstacle to the combinations which their moleculæ tend to form: but the differences which may be offered by positive electricity and negative electricity remain to be determined: the chemical effects of the pile of Volta may be much more considerable than those of the common electricity, although the latter possesses a much greater tension, because its action being necessarily interrupted, the chemical effects which require time to be accomplished can only begin to be effected, and may even be destroyed by the sudden re-establishment of the first state of the body, while the permanence of the action of the electromotive apparatus, although weaker at each instant, may give rise to the chemical changes which it promotes by diminishing the effects of the force of cohesion.

I do not myself consider the explanations I have now hazarded as more than conjectures which observation may confirm or destroy.

NOTE XII.

THE experiments made by Deluc* prove incontrovertibly that the quantity of vapour formed in a vacuum, is the same as if the space was filled with air.

The thermometer being at 65° Fahr. the maximum of the evaporation in a vacuum raises the mercury of a small manometer 0.5 inches, according to the mean result of

* Philos. Trans. 1793.

several experiments made at the same temperature; the recipient being filled with dry air, and afterwards brought to extreme humidity, the barometer, considered as a manometer, will equally experience an elevation of 0.5 inches.

He concludes from a great number of experiments made with his known accuracy, that *the product of evaporation is always of the same nature, that is to say, an elastic fluid which, whether alone or mixed with air, affects the manometer by pressure, and the hygrometer by humidity, without any difference being produced by the presence or absence of air, at least in a sensible manner, as far as is yet known.*

He moreover shows that the hair hygrometer is a deceitful index in the degrees which are near extreme humidity, which confirms the observations I have made on this subject.

The correspondence which exists between the temperature and evaporation made Deluc conclude that the latter was only owing to the action of heat; according to him the difference between evaporation and vaporisation is, that in the latter the vapour must overcome the pressure exercised by the atmosphere on the water, and that in the first the vapour forms at the surface of the water at all temperatures, because there it only meets with a resistance which it can vanquish at all times; it only mixes with the air, and dilates in proportion to its quantity, as if it was a new quantity of air.

NOTE XIII.

After having proved that the phosphoric acid obtained by dissolving calcined bones in sulphuric acid does not retain a sensible quantity of the latter, and that all the sulphate of lime is separated from it by crystallization, provided the sulphuric acid has not been employed in too large a quantity, which for this reason he limits to four parts with six of calcined bones, Bonvoisin shows, as I have said, that the phosphoric acid retains a portion of lime : he has proved that by saturating it with ammonia, a precipitate was produced which was phosphate of lime, as had been before observed by Bergman, and that only part of the lime was precipitated by the ammonia, so that the saturated liquid would yield only a phosphate of ammonia and lime, analogous to the phosphate of magnesia and ammonia made known by Fourcroy : he observed that after the precipitation by ammonia was completed, a new precipitate was obtained by means of the carbonate, which was carbonate of lime, and that thus all the lime held in solution by the phosphoric acid might be precipitated in the state of carbonate, so that he recommends the employment of this process, evaporating and crystallizing the phosphate of ammonia after the precipitation, in the preparation of phosphorus, and to obtain every possible advantage from the phosphoric acid : he is even of opinion that, by this simple means, a perfectly pure phosphoric acid might be obtained, by driving off the ammonia by heat in a silver vessel. These experiments appear to me to be accurate, unless it be that the precipitate by the carbonate of ammonia is not deprived of phosphate of lime, and that the phosphate of ammonia also retains a considerable portion of lime which may be rendered sensible

sible by mixing carbonate of pot-ash or soda with its solution, so that this salt is very suitable for the production of phosphorus; but the phosphoric acid obtained from it is not so pure as that yielded by the combustion of phosphorus, which is afterwards saturated with oxygen by treating it with nitric acid.

Gay Lussac has found a method of obtaining the phosphoric acid, immediately, and still more freed from lime than by the preceding process. This method consists in adding oxalic acid to phosphoric acid, thickened and purified from sulphate of lime; he then mixes a considerable quantity of alcohol with it, which dissolves the phosphoric acid, and leaves the oxalate of lime; nevertheless the tests still show that a very small quantity of lime remains united to the phosphoric acid. It was believed that alcohol did not dissolve phosphoric acid, and Rouelle, who at the time made some interesting observations on the process which was then made known under the name of Scheele,* employed it to precipitate the phosphoric acid from bones which had been dissolved in the nitric acid, after having separated part of the lime by means of the sulphuric acid, but the precipitate obtained was an acidulous phosphate of lime, and, by repeated lotions, might have been reduced into phosphate of lime.

The property of forming a transparent and deliquescent glass is no proof that the phosphoric acid does not retain lime; for Bonvoisin obtained a similar glass from phosphoric acid which he had saturated with ammonia, and from that for which he had employed carbonate of ammonia; now the first still retained a considerable portion of lime, as results from his own experiments, and the latter also retains a portion.

Fourcroy and Vauquelin are of opinion that carbonate

* Journ. de Médecine. Octobre 1777.

of ammonia has not the property of decomposing the phosphate of lime, and of precipitating carbonate of lime: they must have experimented on a calcined phosphate of lime, whose force of cohesion is an obstacle to the action of the carbonate of ammonia; but it was not in this state that Bonvoisin made the decomposition.

I do not yet agree with my learned colleagues on the employment of oxalic acid to precipitate the lime from the phosphoric acid, and by means of which they have endeavoured to determine the proportion of lime in the enamel of the teeth: in this respect I am of the opinion of Bonvoisin, who proves by his experiments that the oxalic acid precipitates only a part of the lime which is held in solution by an acid, and this effect is so much the less as the excess of acid opposed to the formation of the oxalate of lime is greater, since oxalate of lime is soluble in the acids. With respect to the process for preparing phosphorus, experience must decide, by a comparison of the cost, between that of Bonvoisin and that recommended by Giobert, Fourcroy and Vauquelin, and which consists in precipitating the phosphoric acid by the nitrate or acetite of lead, and afterwards making use of this precipitate: nevertheless, that which prejudices me against the latter process is, that the phosphate of lime is soluble in the acids, so that a part may remain in the solution; besides, Trommsdorff affirms that the reduced lead which remains in the retort employed in the production of the phosphorus, is a phosphuret of that metal.*

There must have been a great difference between the acidulous phosphate which I used, and that employed by Fourcroy and Vauquelin, since they say it is *soluble in water with absorption of caloric*, while mine, although prepared in different manners, was never more than solu-

* Ann. de Chim. tom. XXXIV.

ble in part, and divided into two different combinations, as I have stated. On the other hand, Bonvoisin says that this salt is *insoluble in water*.

In the scientific memoir* in which Wollaston has described the substances and combinations found in the human calculi, and which are the lithic acid, whether we ought to consider it as an acid, or, according to the opinion of Pearson, as an oxide; oxalate of lime which characterises the mural calculi; ammoniaco-magnesian phosphate and calcareous phosphate which give a crystalline appearance to some species of calculi, he finds a difference between this phosphate of lime and that which enters into the composition of the bones, and he appears to consider the latter as a phosphate with excess of lime; nevertheless this excess is only owing to carbonate of lime as Fourcroy has pointed out, and whose existence has been directly proved by Hatchett: in fact, lime cannot maintain itself in excess in the midst of other substances which have a sufficiently strong tendency to combine with it.

NOTE XIV.

If the observations which I have offered do not deceive me, when affinity produces a combination, the particular properties of the elements of this combination experience a greater or less saturation, and thus modified give birth to those of the combination: in the substances which have not been in an elastic state, very variable proportions are more particularly established, according to the quantities of them which exercise a mutual action, and

* Philos. Trans. 1797.

according

according to the causes which favour it, or which are opposed to it; the figure of the elements seems to have but a very weak influence on the formation of the combination; on its proportions and on its chemical properties. The form of the integrant moleculæ of a combination, being a result of the reciprocal action of its elements, and of that of caloric, it must be the same, or nearly the same, in combinations of the same species; but it may also be the same in very dissimilat combinations: this is a similar result which may be derived from the reciprocal action of very different substances.

When afterwards the integrant moleculæ exercise a very weak reciprocal action, and tend to collect together in crystals, their figure will have a very great influence, and the results of this weak action will be subordinate to it, and be sufficiently uniform: then arise the particular phenomena of crystallization, and the relations of the structure which have been developed with so much superiority by Hauy; but if the reciprocal action is too brisk, if its effects are too rapid, or if they are counteracted by obstacles, the figure of the moleculæ cannot intervene, and nevertheless the compound substance possesses all the properties which depend on its tendency to combination, or on its force of cohesion.

These principles are contradictory to those which serve as the basis to Hauy's Mineralogical System; nevertheless the profound esteem with which his intelligence and scientific labours inspire me, lead me to enter into a discussion which may serve to establish the communication which chemistry and mineralogy should maintain with each other, and which Hauy himself did not intend to interrupt: in this discussion I shall consider the results of mineralogical observation much more than those collected from insulated chemical phenomena.

In speaking of the method which he has adopted in the
vol. I. classification

classification of minerals, Hauy says, " I determined at first to be guided as much as possible by the results of chemistry. In fact, where can relations be found better calculated to connect the various mineral substances intimately, than those founded on an identical principle? Where can more distinct differences be found between the same substances than those which depend on the principles peculiar to each of them? Now, to class the different beings of the same kingdom, is to establish a continual comparison between them, according to the relations which connect them, and the differences which separate them. This comparison will therefore be the most exact, and, at the same time, the most natural possible, that which will be the least arbitrary, if the method chosen to establish it is that which unveils the intimate composition, and the bases of each substance, which teaches what it is in itself, rather than that which only shows its probabilities, or at most its exterior effects.

" Before going further, let us remark that there are two problems to solve in the present case. The first consists in dividing and subdividing the aggregate of the substances which the method should embrace, so that each may be in its true place in it. This is what is called *Classification*. The object of the second is to furnish easy and commodious means so to characterise each substance that it may be recognized wheresoever it is met with, and be found in the place which has been assigned to it in the method."

It evidently results from these considerations, full of truth, that the chemical properties which characterise minerals will serve, as much as it is possible, for classing them; and, in fact, Hauy established his first division into four great classes solely on the chemical characters.

All the subdivisions should, for the same reason, be founded,

founded; as much as it is possible, in chemical analysis, when this shall be capable of showing their composition, and when properties sufficiently distinct shall not require a particular classification.

But it is soon seen that there are substances which are only a mechanical mixture, while there are others which are in a state of combination; now, although the first may be in as uniform a state as the others, it is clear that they must be distinguished, even though chemical analysis should indicate similar quantities of the same elements.

The composition of a substance whose integrant parts are owing to a combination may be confined to fixed proportions, or it may have a latitude in the proportions which would lessen in a greater or less degree the precision of the method. Observation soon proves that it is the last of these alternatives which occurs in the greatest number of cases, so that in following the most certain guide we cannot attain to a classification which corresponds strictly with the elements of mineral substances, and a precision which mineralogy does not admit of must be abandoned.

Besides, the same composition in minerals may give birth to such different physical qualities that it will be necessary to distinguish them; thus, rock-crystal must not be confounded with silex, although they have the same composition. In the subdivisions, therefore, other characters will frequently be wanting, even for simple substances, or for those whose integrant parts are in a state of combination, but they must be subordinate to the chemical; and in every case it is proper to collect all the marks which are easily recognized, such as those for which we are indebted to the celebrated Werner, to the end that they may be employed as signs of the composition.

tion of a substance, without being obliged to have recourse to chemical analysis.

Among these secondary characters are the forms of crystallization; but what value must be attributed to them? It is on this question that I differ in opinion with Hauy, who appears to me to have given them an importance much too great, and who, neglecting the principles he had at first laid down, establishes his species and his varieties on the relations of structure alone.

After having shown that chemical analysis does not always establish the differences which must be admitted between minerals, which I do not deny, he expresses himself thus: "A character exists much more solid, and, " by its invariability, much more proper; it is that taken " from the exact form of the integrant molecule, because " this form exists without any sensible alteration, inde- " pendently of all the causes which may vary the other " characters.....

" Will it be said that there are forms of the integrant " molecule common to substances of very different na- " tures? I shall in the first place observe that this only " takes place in solids which have a peculiar character of " regularity, so that in all the other cases the form of " the integrant molecule is alone sufficient to determine " the species. I shall afterwards reply, that the greater " number of substances which have a common molecule " (and the same may be said of those which, like the " ductile metals, never have a lamellated texture) are " easily distinguished by other characters: for example, " the cube is the integrant molecule of borated magnesia, " muriated soda, sulphurated lead, sulphurated iron, &c. " all substances which are easily known independent of " mechanical division."

Is it expedient to give so extended a confidence to a character

character which does not show any difference between substances so opposite as those which have been just named, and to which several others might be added? It is said, that, in this case, recourse may easily be had to other characters, and they are taken out of the chemical method, but the conclusion which at once offers itself is, that this method has a greater extent and greater certainty, although alone it is insufficient.

It may be supposed that in simple substances which are naturally in a solid state, the form of the moleculæ has more decisive relations than that of compound substances; but as the same form may belong to different substances, it is still requisite that analysis shall have previously determined the nature of the substance to which it belongs; besides, if this form is indistinct, must we give up naming and classing the substance? and if other properties show that it belongs to a known species, must we conclude that it has a composition such as explains its properties, or be confined to asserting that its moleculæ have such a form; that is to say, that if they could be united by crystallization, they would have produced one sort of crystals?

To show that the integrant molecule is the type of the species, and that the species is uniform in its composition, Hauy is obliged to consider all the differences which analysis finds in minerals of the same form, as heterogeneous matter: he says, "Every thing which precedes
" leads us to an interesting consideration relative to the
" chemical composition of minerals, it is that the prin-
" ciples which concur to form their integrant moleculæ
" must, as it appears to me, be uniform in respect of
" their quantities and qualities; so that the substances
" which occasion a variation in the products of their
" analysis are foreign to the moleculæ, and only inter-
" posed between them in the mass of the mineral." And
he adds in a note, "I also think that in those cases in
" which

" which it is said that there is an excess of one of the principles, in other respects essential to the composition of a mineral, the superabundant part stands for nothing in the formation of the molecule, and must be placed among the heterogeneous substances purely accidental." *Tome I.* p. 161.

According to this doctrine chemical combinations are only made in determined proportions, and all that is found in a combination out of these proportions is only a mixture of heterogeneous substances, and which do not contribute by their affinity to the state, or properties of the combination; in fact, this supposition, which cannot stand against chemical observation, is necessary to maintain that the form of the molecule is the type of each species, and that this is a uniform combination.

In consequence of these principles, Hauy considers the colouring particles of some minerals, for instance, those of the oxide of chrome which colour the emerald green, as simply disseminated in such a way that they do not injure the transparency. *Tome IV.* p. 415.

The uniformity in the composition, notwithstanding the difference of the specific gravity of the elementary parts; the transparency, which proves that they no longer exercise a separate action on the rays of light; the properties which are in common, but different from those of the separate elementary parts, are nevertheless undeniably indications of combination.

All the characters of a combination are unquestionably found in glass, which may be composed of very different proportions, and it cannot be asserted that this combination has determinate proportions, and a form which belongs to its integrant particles, and that all the rest is interposed without entering into the formation of the compound. What I now observe of glass is applicable to all the transparent minerals which contain oxides or other elements

elements foreign to those to which the form of their integrant molecule is attributed.

By a consequence of the preceding principle, Hauy says, *Tome III. p. 243*: "I conceive that the granites, " gneiss, &c. the mixtures, may pass from one to the " other; but it is not so with the species, properly so " called; if unfortunately this was the case we should " have only a series of darkness; mineralogy would be- " come a sort of labyrinth wherein we should be unable " to find the way, and would be every where full of pas- " sages which do not lead to any thing."

Daubuisson, who testifies for Hauy all the veneration which is due to him, observes on this passage: "that in " our laboratories we combine gold and silver at pleasure, " and that the mixture forms a mass entirely homoge- " neous which has its peculiar characters. Nature can, " and actually does, make similar ones: we find pure " gold, gold mixed with a little silver, the relative quan- " tity of the latter augments successively by degrees, we " finish by having pure silver." He quotes other exam- ples taken from mineralogical observation.*

Even the salts which are the most uniform in their proportions may be surcompounded, or combine together without their crystalline form or their transparency being altered; they may vary in their proportions, without their form undergoing any change, as, with the same compo- sition, the form of the integrant particles may be dif- ferent.

Leblanc† combined oxide of mercury with muriate of soda, so that a little more than twelve grains of oxide united with an ounce of the salt, which by crystallization yielded cubes and tremiae, like the common muriate of soda,

* Journ. de Phys. tom. LIV.

† Ibid. tom. XXXI. p. 95.

We cannot here deny the reciprocal action, which not only renders an oxide soluble, not so in itself, but maintains it in the same combination with muriate of soda, notwithstanding the great difference of their specific gravities. A solution of equal parts of sulphate of iron and sulphate of copper yields tetrahedral rhomboidal prisms of a greenish blue : the form of these crystals is perfectly well determined, and the homogeneity of their substance is easily discoverable by the naked eye. It may be dissolved and crystallized repeatedly, without the substance, or the configuration of its crystals being in any way changed..... A mixture of three parts of sulphate of iron and one part of sulphate of copper, gives crystals of an emerald green, and of the same form as the preceding; some difference in the colour alone distinguishes these two species of surcompounds.

Vauquelin has shown that sulphate of alumine contained indifferently seven parts in a hundred of pot-ash or of ammonia, without any difference being perceived in the crystallization : the proportion of acid itself may be changed, as I have ascertained, and Leblanc has proved that the sulphate of alumine might be surcompounded with a considerable quantity of sulphate of iron, and, nevertheless, by crystallization, furnish regular octohedra.

Although chemists have hitherto neglected to pay particular attention to the forms of surcompounded salts, it would be easy to accumulate observations which prove that salts may be surcompounded without experiencing a change in their forms correspondent to the surcomposition; and nevertheless these surcompositions which preserve their transparency are the effect of the reciprocal action of the elements which compose them.

If this truth is incontrovertible with saline substances which have a considerable solubility, and which consequently

quently experience an energetic action with respect to their force of cohesion from the water, the reciprocal action of substances which have little solubility will be much more efficacious to unite them in a state of combination.

It is not therefore astonishing that there are found in minerals considerable variations in the proportions of the elements which compose them, although they offer the marks of a complete combination, such as the transparency; and to deny the reciprocal action of the constituent parts in these combinations would be to rest on an arbitrary system.

Thus, in the analysis of granite given by two chemists equally remarkable for the accuracy of their inquiries, Klaproth and Vauquelin, there is a difference which is very far from what might be attributed to the processes; their determinations vary in silex from 54 to 36; in alumine from 28 to 6; in oxide of iron from 41 to 10. De Lametherie relates other similar examples.*

There are also combinations to which one of the principles gives the form which is peculiar to it, although it is in a smaller proportion than the others: thus the gypsiferous muriated soda retains the appearance of muriate of soda, and, like it, divides parallel to the faces of a cube, *Tome II. p. 365*; although according to Klaproth's analysis it contains 31.2 of muriate of soda, 37.8 of sulphate of lime, and 11 of carbonate of lime in the 100 parts.

Red sulphurated arsenic seems to have the same primitive form as the sulphur, although only a tenth of the latter enters into the combination; this has led Hauy into a reflection which it is difficult to reconcile with the principles he has followed. "The question therefore is

* Journ. de Phys. tom. LIV.

" to

" to know whether the principle which should be attended to in the classification is that which is most abundant in a substance, or that which marks it with its form." *Tome IV. p. 233.* It seems to me that he ought to have decided on this leading point before establishing a mineralogical system on the opinion that the form of the integrant molecule is the type of the mineralogical species.

The consideration of the crystalline forms has not only the inconvenience of bringing substances together which are separated by their composition, but it has also a more serious one, that of requiring the separation of substances, which analysis proves to be perfectly identical, into different species: thus the analyses of the aragonite, by Klaproth and Vauquelin, showed that it was a calcareous carbonate; Thenard resumed the analysis, and employed every means furnished by chemistry to discover the other substances which might be found in it, and he ascertained, not only that the aragonite is a carbonate of lime, but also that the relation between the acid and the base is the same in this carbonate as in that known by the name of *Iceland Spar*.

" If, says Hauy, this was the limit of chemistry, we must conclude that the difference of about $11\frac{1}{2}^{\circ}$, which exists between the primitive angles of the two substances, and which indicates a considerable one between the forms of their integrant molecule, is an effect without a cause, which sound reason disavows: it is rather to be presumed that new researches will produce that agreement here which, hitherto, has uniformly reigned between the results of chemical analysis, and those of the geometry of crystals." *Tome III. p. 347.*

Hauy rests upon the supposition that some foreign matter is in this mineral, which is of a composition so simple and so easy to ascertain, and which has been treated by

the

the most able chemists; but what inference can be drawn from thence, unless that a very trifling circumstance may, in some cases, produce a change of form, as will be seen in the following example, while very considerable differences in the composition may be met with under the same form?

Vauquelin has proved by experiments, which it will be sufficient to mention appeared to him to be convincing, that the anatase and the oisanite are the same substance, and that both these minerals arise from the oxide of titanium. "It remains still to be examined, says he, if the forms of these two minerals can be reduced to the same primitive type; but, according to the observations of Citizen Hauy, these forms are incompatible."*

The anhydrous sulphated lime experiences a mechanical division which is made with equal freedom in every direction, and leads to integrant moleculeæ of a cubic form, or very nearly so. *Tome IV. p. 349.* Hence it results, "that on comparing this substance with the common sulphated lime, before their chemical composition was known, it might have been pronounced before-hand that they must constitute two different species."

Chemical analysis, which here meets the approbation of Hauy, proves that there is no other difference between these two substances but in the water of crystallization, of which the anhydrous sulphate is deprived; and nevertheless the water of crystallization exercises only a very feeble action in comparison with the reciprocal action of the sulphuric acid and the lime, so that it easily yields to the action of caloric, and abandons the other two principles. There cannot be found in this water, admitting that the consideration of the chemical properties are entirely neglected, a difference which authorizes the

* Journ. des Mines. No. LXV.

making

making a distance between these two substances, greater than between the carbonate of lime, and the ferriferous carbonated lime, and equal to that which is established between carbonated lime and sulphated lime.

An observation of Lowitz shows the great influence of water on the accidents of crystallization, although it exercises but a very weak chemical action, and consequently contributes very little to the characteristic properties of a substance.

By exposing a solution of muriate of soda to great cold, Lowitz obtained crystals of an hexagonal form, which were two inches in diameter and a line thick, which dissolved into a liquid at a temperature some degrees below zero, and which fell into a very fine and very white powder at a very cold temperature.*

I have spoken (*Note I.*) of the differences of crystallization which Davy observed in the nitrate of ammonia, according to the temperature he employed.

Hauy finding himself obliged to restrain the indication of the species by the form of its integrant molecule, although he considers it as the type of the species, because some of these forms are common to substances of a different nature, when they have a particular character of regularity, *Tome I. p. 159*, makes chemistry intervene, and determines to define a species in mineralogy, *a collection of bodies, whose integrant moleculæ are similar, and composed of the same elements united in the same proportion*; but it is sufficiently obvious from the passages which I have quoted, that he has frequently deviated from this principle, although substances endowed with a particular character of regularity were not in question; and in fact how could he have confined himself to it, since chemical analysis and the form of the integrant moleculæ so often

* Ann. de Chim. tom. XXII. p. 27.

give opposite indications. He was obliged therefore to choose between analysis and the form of the integrant moleculæ.

Although analysis is the only means calculated to show the composition of minerals, as Hauy himself has stated; I nevertheless repeat, that they cannot by its means be distinguished into species, constant and uniform in their composition, because this composition may vary, although the properties which ought to be considered as characteristics do not authorize their separation, and, that in their classification they must not be restrained to it alone, because it would confine it within too contracted limits, and, besides, it is not sufficiently advanced, to satisfy the demands of mineralogy: but the uncertainty attendant on analysis is much more limited than that which the form of the integrant moleculæ carries with it, if it is absolutely necessary to choose between them exclusively, independent of the contradictions offered by the two results. Whence then arises this uncertainty attached to mineralogical methods? Does it depend on the imperfection of the science, or on the nature of the substances which are the objects of it? Without doubt mineralogy cannot outrun the progress of analysis, but in my opinion a mineralogical species, such as it has been conceived by Hauy and by Dolomieu, can only be realized in so small a number of substances that it is impossible to establish the distinction of minerals on such a foundation; and it is from having made an imaginary definition that they have been led into exaggerated principles, and that observation disproves them. De Lametherie appears to have made very just reflections on the insufficiency of form to indicate the species; on the properties which should be employed to distinguish them; and, on the gradations which lead from one to another.

His predominant idea has led Hauy to establish varieties

ties in mineral substances, according to the accidents he met with in the secondary forms of crystallization, whatsoever might be their chemical character: thus he describes and names forty-seven varieties of carbonated lime; *the primitive, the equiaxe, the inverse, the metastatic, the contrasting, the mixed, the based, the inimitable, the birhomoidal, &c.* Tome II. p. 132. Adjoining these varieties is found the ferriferous carbonated lime, which is divided into *primitive, equiaxe, inverse, contrasting, based, dihexaedral*. This ferriferous carbonated lime frequently contains only a third of its weight of calcareous carbonate, the remainder is oxide of iron with more or less oxide of manganese. Here then is a mineral which analysis proves to contain a considerable, and even a predominating quantity of a substance very active in its properties, of a metal, which, for its utility in the arts, it is important to recognize, and yet its nature is no better designated in the system than as the smallest variety of a secondary crystallization.

The error of the system is also shown in the most striking manner in those substances which have a simple and invariable composition, and which may be known by a very easy chemical assay, and, which is almost always inevitable, nevertheless experience some variations in their crystallization. I shall take as an example the sulphate of magnesia or sulphated magnesia: although this salt has an invariable composition, it is nevertheless divided into *bis-alternate, pyramidal, triunitarian, trihexaedral, equivalent, plagiedral*, and how might this division, and these denominations, be multiplied, were we to amuse ourselves in varying this salt by all the means which are capable of influencing it !

While these slight variations of form were described, which are very interesting when the end is to prove the laws of crystallization, but which are useless to the knowledge

ledge of the object, the amorphous minerals, which are more constant in their composition and in their properties than some regular crystals, were excluded from the mineralogical system. Daubuisson cites as an instance the Klingstein of Werner, "which has been found in America forming the masses of mountains with pointed summits, such as those which are seen in Bohemia, in Silesia, in Scotland, in the Valais, &c. It was every where the same stone, every where placed in the same manner, every where affecting a similar form, and offering the same characters; thus, this is sufficient to entitle it to a particular name to distinguish it from other stones.....It is said that crystals are the flowers of minerals; but immense forests should be taken for something."

I go no further than the preceding observations, because they seem to me to prove that characters taken from the form of substances are not by themselves sufficiently sure and constant guides to lead us to the knowledge of the nature of minerals, and to their classification.

The choice of these characters necessarily causes a great number of useless divisions, and introduces new denominations which have no relation with the intimate properties, not only in the varieties, but also in the species, such are *the mesotype*, *the harmotome*, *the grammate*.

Thus mineralogy, in contradiction to other sciences which in their progress perfectionate and simplify their systems, becomes more rugged with difficulties which do not elucidate the properties of minerals. What has been learnt on the properties of the carbonates of lime by the laborious study of the geometrical forms of forty-seven known varieties of crystals of this substance? and notwithstanding the number, little progress has yet been made,

made, since the number of possible crystals is much greater, and since observation will successively bring forth new ones: in fact, these toilsome investigations have hitherto only led to one indication interesting to mineralogy, that of the identity of the composition of the emerald and of the beryl, which has been ascertained by Vauquelin, and which is connected with the discovery of a new earth.

This method has also the inconvenience of only being applicable immediately to substances which have a regular crystallization, and with respect to the others, if they have no continuity with the first, they can only be determined according to Hauy, *Tome I.* p. 159. by characters less sure than those taken from the structure. It must be confessed that chemistry would be confined within very narrow limits if it had no other dependence than the relations of structure to decide on the nature of the substances which it examines, and nevertheless the object of chemistry and of mineralogy is, in this respect, the same.

NOTE XV.

To establish simple rules that chemists might follow a uniform direction in the choice of denominations by which they could designate the results of their inquiries; to indicate by these denominations the substances which have an analogy of composition; to designate the elements on which the attention should be fixed, in the different combinations produced by their mutual action; to announce clearly, and without tedious circumlocution, the products of complicated operations, are the advantages which the authors who proposed the chemical nomenclature

nomenclature had in view, and by the use which has been made of it they seem to be irrevocably confirmed, as well in instruction, as in the works which offer so great a number of new objects to impress on the memory, and to submit to discussion; but their first attempt could not be without imperfections, and they were far from concealing it.

It is particularly by the composition of words which designate combinations, and by the terminations which show their analogies, that the proposed object must be fulfilled, and it is this part of the nomenclature on which it is important that chemists should be agreed.

Respecting the denominations of simple substances, or of an indeterminate composition, it seems to me not only that words, insignificant in themselves, should not be rejected, but that they are the best calculated to accomplish the object, provided they are capable of the combinations of the nomenclature.

They are proper names, whose application must be learnt by a knowledge of the object; they connect themselves with this knowledge, which is indispensable, and recall it to the mind: no difficulty arises from the words lime, iron, magnesia; it is only when one of these words, applied to a determinate substance, is afterwards employed to express the habitude of another substance of which it would give a false idea, that it becomes a vitiated denomination: thus, the word lime applied to oxide of iron, would occasion an error on the properties of the substance, and produce a disagreement in language.

It was necessary therefore to change some names which were founded on erroneous properties, and to choose some to indicate substances which before were little known: among the properties of such substances those were sought to form the new denominations which seemed best calculated to designate them; but it was the words

formed in this manner which, although but few, occasioned the most discussion, and gave rise to the most opposition: these were the objects of those vapid pleasantries with which the methodical nomenclature was loaded at its first appearance, in the *Journal de Physique*, in which they find the etymology ill founded; in which they wish to substitute another property to that which was chosen. When they do not agree to reform a word, they endeavour to support its signification in the compound words to which it must be applied: if they find that the etymology is established on some inaccurate property, even in a foreign language, they reject it: thus, because *tungstein* signifies a heavy stone in German, they propose to substitute the name of *Scheelin* to that of Tungsten, which has been long received to express a particular substance.

Chenevix, who has just published a very philosophical work on the principles of nomenclature,* and of which I hasten to profit, is, in my opinion, too anxious to preserve the precision of etymology in the combinations of the nomenclature, although he gives the preference to denominations which are not possessed of it.

It seems to me that the common interest of chemists requires that they should follow the same practice with denominations taken from a known property, and with those which are not so; that if they have recourse to etymology to obtain the acceptance of a new denomination which a discovery renders indispensable, they should omit it entirely as soon as it is adopted, and make no use of it in the combinations of words, but what may be called mechanical: the chemist who establishes it must direct his attention more to Euphony, and the conveniences of nomenclature, than to the indication of a property.

* Remarks upon chemical nomenclature, 1802.

Do we not, in fact, see expressions, whose etymological application has become false, continue to fulfil their functions with the same advantage? Does not the eudiometer give an idea of the instrument, or of the process, by which the proportion of oxygen in atmospheric air, or in another gas, is determined, although we are well convinced that it does not indicate the salubrity which was employed to give a name to this instrument? Are the designations of brown, white, or black, applied with any obscurity to the products of those substances which a quality has caused to be designated by these names?

I might perhaps justify the authors who proposed the nomenclature for having deviated in respect of the nitric acid from the rule which they followed in the denominations of the sulphuric acid and the phosphoric acid, by the difference of properties which the nitric acid offers in the different combinations; but though this might have been the case at the time the nomenclature was proposed, I think it right to retain the denomination of azote, independently of the motives which made them choose it, because it is the most generally adopted, and because it classes well in the combinations of the nomenclature.

If it is wished to substitute the word nitrogen, proposed by Chaptal, for azote, because, as applied to the nitric acid, it would be analogous with those by which the substances are designated which are considered as the sources of water and the acids, would not some one observe that it is rather the radical of ammonia than of nitric acid, and think it wrong to leave ammonia, the powerful alkali, without a radical, or that it should be considered as composed of nitrogen or of hidrogen; of two generative substances which announce compounds that are at so great a distance from it.

In the combinations of words I only introduce mechanical abbreviations; thus, by hidro, I mean hidrogen; by

oxi, oxigen : according to this explanation, Chenevix will see that by the word oxi-carburated hidrogen I intended only to designate a substance composed of hidrogen, oxigen, and carbon, and that I did not wish to give it an indication of acidity: when I proposed to designate the combination of sulphurated hidrogen with a base by hidro-sulphuret, I lost sight of the proper meaning of the word hidro, and saw in it only a diminutive of hidrogen: I have proceeded in the same manner in the designation of the other states of the combination of sulphur and of hidrogen: I acknowledge that these denominations have the inconvenience of not being sufficiently distinct, but it is difficult to avoid it, because the combinations themselves are only distinguished by weak characters; nevertheless these designations avoid the circumlocutions which themselves would not be free from obscurity, and they indicate states of combination which it is essential to distinguish.

In other respects I adopt the observations of Chenevix on the construction of some compound words, in which the principles which have been established to indicate the analogy of combinations have been neglected: with him I call the combination of hidrogèn and carbon, carburated hidrogen, which is analogous to sulphurated hidrogen, and I have already made a similar reform in the denomination of phosphurated hidrogen.*

He makes observations which appear to me to be very just on the state of a vegetable substance which becomes acid, and which cannot be considered as the radical of this acid, like the phosphorus and sulphur, in the acids which they form. They should therefore all have a uniform termination. That in *ic* being the most general should be adopted in all, more especially since it has been proved

that the acetic acid should not be distinguished from the acetous acid; so in this treatise I retain only this denomination; nevertheless I make no difficulty of preserving that of tartareous acid, because, in French, it is more conveniently applied to its compounds, and is generally received.

In general I attach less importance to the strict observation of the principles of nomenclature, which, in reality, are only agreements, into which several considerations may be introduced: the essential point, in my opinion, is to compound the words so that they leave nothing equivocal on the parts which enter into the composition of a combination, and on the relation of its characteristic properties with those of other substances.

When a species of combination is not subject to proportions which limit the properties, the nomenclature is necessarily indefinite, as to what is in the composition, and in the knowledge which may be acquired from it; thus, in the oxides, only the two extremes can be defined with precision: the word oxidule, employed by Hauy, may be adopted for the slightest degree of oxidation, but the intermediate states must be indicated by the colour, or by some other accident.

It is a danger common to the nomenclature, and to the science of which it is an instrument, to place imaginary barriers in the composition and in the designation of substances. It is thus with Brugnatelli, who on distinctions, often ideal, proposes the thermoxigen, which he distinguishes confusedly from oxigen, the oxides, the thermoxides, the oxiques, the phlogogen, &c. He pretends that these innovations have begun to be established on the banks of the Thames, but Chenevix, who pauses to object to some of them, tells us, in the name of the chemists his compatriots, that Brugnatelli was misinformed respecting its progress; this cacophony in words and ideas must

must not be heaped upon the learned chemists who at present honour England in so great a number.

I must justify, by some examples, the judgment which I have pronounced on the nomenclature of Brugnatelli. The process by which phosphorus is reduced into phosphoric acid by the action of nitric acid, and the simple explanation given of it, are known. Brugnatelli gives this operation, which he has complicated with alcohol in the following manner :

It is said in a note communicated by him,* " Brugnatelli has found an easy and quick method of obtaining the oxiphosphoric very pure and concentrated, by the decomposition of the thermoxigen of the oxiseptonic in the cold.

" Knowing that the oxiseptonic is partly decomposed " at the instant when it comes in contact with alcohol, " and changes the proportions of the thermoxigen with " respect to the other component parts of this oxique; " he seized this moment for presenting phosphorus to the oxiseptonic. This oxygenable combustible then de- " composes the thermoxigen of the oxiseptonic, and is " changed into oxiphosphoric. For example, let half a " grain (gros) of phosphorus be plunged into about two " grains of alcohol, contained in a glass; afterwards let " half an ounce of concentrated oxiseptonous be poured " over it, &c."

Brugnatelli gives the name of *ammonure* to combinations of the oxides with ammonia, and this termination in *ure*, according to the received stipulations, ought only to be applied, as has been well observed by Chenevix, to combinations of combustible substances : now there is not any known combination of metals with ammonia,

* Journ. de Van Mons.

though there is of the oxides which are no longer combustible.

The error of Brugnatelli is not solely confined to this false denomination in the description which he has given of the ammoniures of mercury and zinc,* but he has also supposed that of mercury in a circumstance in which it did not exist, and he has described as new that of zinc, which Lassone made known long ago. He prepares his pretended ammoniure of mercury in the following manner :

" To obtain this ammoniure, mercury is dissolved in " sulphuric oxique, and evaporated to concretion; there " remains a mixture of neutral sulphate, of acidulous " sulphate, and of mercury; the latter is separated by " means of cold water; the saturated solution is diluted " with half its weight of water, and precipitated with " liquid ammonia; a very abundant white precipitate of " oxide of mercury is formed." It is this precipitate which he dissolves in ammonia to form the ammoniure of mercury, but Fourcroy proved long since † that the white or grey precipitate which was obtained was not the oxide of mercury, but a very variable combination of this oxide with a certain proportion of sulphuric acid and ammonia, and that by the addition of ammonia it is not an ammoniure which is obtained, but a combination differing only from the preceding by having a larger proportion of ammonia.

* Journ. de Chim. par Van Mons. Vendem. An. X.

† Mém. de l'Acad. 1790.—Ann. de Chim. tom. X.

NOTE XVI.

COUNT RUMFORD has published several memoirs by which he has endeavoured to prove that liquids and elastic fluids are not conductors of heat, and that they only transmit caloric by means of the contact with solid bodies which is owing to the motion of their parts: as this property would make a difference between the states of a substance, much greater than there is occasion to suppose in the explanation of the other phenomena; as, besides, this celebrated philosopher has fixed the attention on an object which had been neglected, and has drawn applications from it, beneficial in the arts and in the uses of life, I think it right to offer some doubts on the principles which he has deduced from his observations. I shall, in the first place, examine whether the facts on which he rests cannot receive a natural explanation from the properties which I have already analysed, or whether it will be necessary to have recourse to particular properties; but I shall only attend to the considerations which may serve to elucidate this discussion, without introducing the details it would require if I purposed examining it more fully.

The experiments which the author made were performed with an apparatus, of which it will be proper to insert a description. "He employed a cylindrical glass "jar of 4.7 inches in diameter, and 13.8 in height; he "put a known quantity of water (about two pounds) into "the jar, which was intended to form a cake of ice at "the bottom of the vessel. For this purpose, the jar "with the water was put into a frigorific mixture of salt "and ice, the action of which was not long in convert-
"ing

“ ing the water into a solid disk adhering to the bottom
“ and sides of the jar; the jar was then removed, and
“ plunged into a mixture of ice and water, to the level
“ of the interior cake, which gave it the temperature of
“ melting ice, or of the zero of the common thermome-
“ ter. Then, after having covered the surface of the
“ ice with a disk of paper, hot water was poured on it, as
“ gently as possible, to about the quantity of 74 ounces;
“ this water was about 8 inches above the surface of the
“ cake.

“ The paper was then removed very gently, and, after
“ having suffered the water to remain a certain number
“ of minutes in contact with the ice, it was poured off,
“ and the jar with the ice which it still contained imme-
“ diately weighed; its difference from the primitive
“ weight established the quantity of ice which had
“ melted while the hot water remained above it.”*

Having observed that the motion occasioned by pour-
ing on the hot water produced an effect which was consi-
derable and foreign to the communication of heat, the
author successively devised several modes of diminishing
it. “ He introduced the hot water through a wooden
“ tube, closed at the bottom, and pierced laterally with
“ several small holes, through which the water issued
“ upon a wooden disk also pierced like a sieve, and float-
“ ing on the water as it rose in the vessel. This disk was
“ removed as soon as the water was poured in, and the
“ vessel was covered with a wooden lid, in the center of
“ which was suspended a thermometer; finally, by pre-
“ viously covering the ice with a stratum of cold water
“ about half an inch in thickness, on which the perfo-
“ rated wooden disk floated, the author succeeded in
“ greatly diminishing the irregularity of the results.”

* Bibl. Brit.

Besides

Besides these precautions, the author separated from his results the quantity of ice which liquefied at the first instant, and which exceeded that which melted in the succeeding spaces of time: in these different experiments, while that part of the cylinder which contained the ice was kept constantly at the temperature of melting ice, the upper part was left in contact with the surrounding air, or surrounded with a bad conducting substance, or plunged into the mixture of water and ice: the water poured on the ice received different temperatures. I make three divisions of the results of all the experiments: 1st. water which was only about four degrees above zero melted a little more ice in the same spaces of time than boiling water: 2d. when the upper part of the cylinder was wrapped in a bad conducting substance the hot water melted more ice than when it was in contact with the air: 3d. when the upper part of the cylinder was plunged into the mixture of ice and water, more ice was melted than when it was left in contact with the atmosphere at 61° Fahrenheit's thermometer.

To explain these observations the properties which we have recognized in liquid substances, and in elastic fluids, and from which we have inferred the changes which are effected in their different states of combination, must be applied to the phenomena observed by Rumford.

We have seen, 1st. that the liquid particles entered so much the more rapidly into combination as they were at a greater distance from saturation, because then the force which solicits the saturation is greatest; so that the effects which depend on the communication of the temperature must be very weak, when the differences between them are but small.

2d. The locomotion which serves to bring together the moleculeæ which are at a greater interval from saturation, accelerates the effect of the reciprocal action by which its equilibrium

equilibrium is established, so that it is necessary to separate the effect which depends on it, from that which is owing to the immediate communication.

3d. Water and some other substances acquire a greater specific levity on approaching the term of congelation, whence it results that the locomotion produced by the variations of temperature in other circumstances will experience modifications, which must be appreciated when water and the liquids which possess this property in common with it, approach the term of congelation.

To apply these properties we must also take into consideration the direction which is given to the emanation of the heat; for the combination of effects will be different according as it arrives by the inferior part of a liquid, or by the superior part.

That a ready motion may be established between the particles which are at the bottom of the vessel, and those at the surface, there must be little difference between their temperature; then the particles which are near the ice, and which acquire expansion, raise themselves above those which have a temperature barely greater; but if the temperature introduces a great difference between the specific gravities, this motion will be much more confined, so that the ice remains surrounded with water of its own temperature, or which is very little removed from it: it is evident therefore that that part of the effect which depends on the motion will be much less when there is a great distance in the temperatures; but when this distance exists, the result belonging to the communication of the heat, independent of the motion, will vary according to the manner in which the temperature is preserved in the liquid: if it has a non-conducting covering, the heat being retained, a greater quantity of it is communicated than if it passed into the surrounding bodies; but if the difference of the temperature of the liquid is not sufficiently

ficiently great, as in the experiment in which water at 16° was employed, it is more advantageous to augment the effect owing to the translation of the particles, by cooling all the cylinder, than to preserve that which is owing to the simple communication of caloric. It appears to me that this explanation flows naturally from known properties, and that Rumford's observations do not lead to new inductions.

It must be remarked, that by separating the effect which took place at the first, when a considerable difference in the temperature could occasion a quick communication, he only observed that which was produced when there were but very slight differences between successive strata of the liquid and the ice itself: now, when there is but a small difference of saturation, either between chemical combinations, or between the temperatures, the equilibrium is established very slowly, and it becomes difficult to appreciate the effects.

The experiments which Rumford made by plunging a small cylinder of iron, heated to the degree of the ebullition of water, into water and mercury standing over a small piece of ice, without producing its liquefaction, only prove that when two bodies differ but little in their temperature the equilibrium is established with difficulty; for it must be observed, that the iron, which had but a little specific heat, and is a good conductor, must have lost the greatest part of its heat rapidly, in that part of the liquid which it passed gently through, and nevertheless have raised that of the liquid but little, or even that of the mercury, considering the mass of it.

But in these experiments of Rumford I find proofs of the property which he denies to liquids.

1st. In all the experiments which I have quoted, except in those made with the heated cylinder of iron, the liquefaction of the ice took place in a considerable degree,
and

and each part liquefied supposes a quantity of heat which would have raised an equal weight of water from the term of congelation to 75 degrees of the centigrade thermometer.

2d. He froze the water at the surface of mercury cooled by a frigorific mixture: the temperature of the mercury was therefore communicated to the water, and the latter yielded its caloric to the mercury, to replace that which it lost.

If the communication of heat was only the effect of the motion of the particles of a liquid, the mercury of a thermometer would scarcely change its temperature when it had arrived at the freezing point of water: in fact, in several of his experiments, (*Essay 7*), Rumford supposes that at this degree the mercury no longer communicates heat: now a thermometer takes the temperature of neighbouring bodies very rapidly, and indicates it several degrees below the freezing point of water, and as far as its own congelation; then it conducts itself like the solid bodies, and its dilatations become proportionably smaller than the preceding.

Rumford has proved that the conducting power of mercury is to that of water as 1000 to 313.

This effect of the mercury, which takes the temperature of the system in which it is placed more rapidly than the water, although it has a much greater specific gravity, although it is much less dilatable by the same degrees of heat, and consequently the heat will cause much less locomotion in its particles than in those of water; this effect, I say, proves that the changes of temperature do not alone depend on the immediate communication, and the changes of the specific gravity which produce the approximation of the particles of unequal temperatures, but also on the better or worse conducting property of each substance.

3d. Rumford

Sd. Rumford paid no attention to the radiant caloric, nor did he make any allowance for it; nevertheless the communication of heat established by its means between solid bodies and liquids, through the gases, cannot be doubted, and it may be remarked that when he brought a heated bullet near to ice and tallow, a communication of heat took place which melted the surface of both without it being possible to attribute this communication to a circulation such as he thinks is necessary.

The ingenious experiments of Rumford have employed the talents of several philosophers who have already proved that the principles to which they led were not conformable to the true results of observation.

Nicholson, in conjunction with Pictet, made some experiments, by which he proved that on heating a liquid at the surface, by the superposition of a body, the heat penetrated, and raised a thermometer placed at the bottom of the liquid: to avoid the communication by the sides of the vessel a bad conducting substance was made choice of, and he ascertained by means of a thermometer placed in the same liquid near the side of the vessel that no current was established which differed in the temperature: finally, the motion of the bubbles which were disengaged, and the other appearances of the liquid, convinced him that currents were not formed.

In these experiments * it was proved that liquids were different in their conducting faculty: the penetration of the heat from the top to the bottom was five times slower in oil than in mercury.

Rumford supposed that the slightest changes of specific gravity were accompanied by a locomotion, which he endeavoured to render visible by exposing an alkaline liquor, in which were suspended very small fragments of

* Bibl. Brit. tom. XVIII.

amber, which he found had the same specific gravity as the liquid, to a change of temperature: but Thomson has shown* that the motions observed in these moleculæ were illusory, and that, in the variations of temperature which are gradual, they appear to be only owing to the difference of specific gravity which they acquire, and to the adherence of air-bubbles, so that some of these moleculæ move in contrary directions, and run against each other without following the direction of the currents: he has also shown that these floating corpuscles might receive different motions, while the strata of the liquid maintained a perfect tranquillity: into a glass vessel he put water tinged blue by juice of red cabbage, he afterwards poured clear water on it, with great precaution, and by means of a tube with a capillary extremity; thus he kept the two liquids separate and distinct, he then heated the vessel gently at the bottom; it is manifest that if a current had been established it would have been marked by the coloured liquid, but the separation of the two liquids was preserved unconfused; moreover the corpuscles put into the first liquid moved upwards and downwards and crossed the line of separation, without producing the mixture of the two fluids, so that their various motions were not the effect of a current which carried them forward, nevertheless the heat was communicated to all the liquid. The propagation of the heat, and the agitation of corpuscles which have nearly the same specific gravity may therefore take place independently of the circulatory motion, which is only established when there is a difference of temperature of a certain intensity between the different strata of a liquid.

Murray has opposed Rumford's opinion with experi-

* Nicholson's Journ. February 1802.

ments still more direct, and not less conclusive;* he placed the bulb of a thermometer in a cylinder of ice, which he filled alternately with oil and mercury; he afterwards brought a heated body near the surface of the liquid; the thermometer rose several degrees in both experiments, but the heat could not have been conveyed by the sides of the ice whose surface would have absorbed it by liquefying: no current was established, for the moleculæ of the liquid, having become lighter, could not take a contrary direction, and the author avoided using water which contracts on passing from the degree of congelation to a temperature a little more raised: the heat must therefore have been communicated to the bulb of the thermometer, without the current, which is supposed to be requisite, being established, and that which served to dilate it was only the excess of what had liquefied part of the ice.

The observations of Murray prove at the same time that mercury is a much more effective conductor of heat than oil, for the elevation of the thermometer was manifested by its intermedium in a much shorter time, and more ice was liquefied.

I am of opinion, that the experiments of Nicholson, of Thomson, and of Murray, leave no doubt on the communication of heat between the moleculæ of liquids: some of them show that the motions of the solid corpuscles which are agitated in a liquid may often be deceitful with respect to the currents which are believed to be perceptible, but their existence must not, for this reason, be denied when a difference between the specific gravities is suddenly established, and when the heat is communicated by the lower part of a vessel: the others prove that the communication of heat may be made through a liquid

* Ann. de Chim. Floreal. An. X.

in which no current can be supposed to transport it immediately to a solid body, and they prove that liquids are possessed of a conducting faculty which differs in its intensity, but it is not to be inferred from this that the locomotion of the particles of liquids does not contribute to establish an equilibrium of temperature more speedily: it is even probable that the latter effect is generally the greatest.

The foregoing considerations, into which I have admitted the application of the faculty of communicating heat common to all bodies, of the conducting difference, and of the more speedy distribution of heat by means of the difference of the specific gravity which it introduces between the particles of a fluid, seem to me to account for all the phenomena which the discernment of Rumford has made public.

These considerations lead me to an opinion very different from his: it is known with what rapidity the thermoscopes, or air thermometers, indicate the variations of temperature: Pictet could not observe a second of difference between the elevation of a thermometer of this description, and the emanation of radiant heat by a body placed at a distance: it has been observed that aerostats experienced a sudden dilatation by the appearance of the sun;* these phenomena seem to me to indicate that the elastic fluids, far from being bad conductors, on the contrary, receive the temperature of other bodies very quickly; for, can it be supposed that all the particles of the gas take the temperature which they acquire by the contact of the covering of the balloon alone, and how can it be conceived that the lower particles, which are contiguous to that portion of the covering which does not receive the solar emanation, should be carried towards

* Descrip. de l'aérostat de l'Acad. de Dijon.

that which is exposed to it? And since these molecules, at each contact, only receive a part of the temperature to which they attain, what a prodigious whirlwind must there be supposed to be in the gas!

It appears to me, that the elastic fluids, instead of being bad conductors, possess this property in a high degree, although they probably differ from each other in this respect; and if air which is confined produces effects which seem to prove the contrary, they are owing to some circumstance which modifies this property.

I think it is probable that this circumstance is the state of compression produced in a gas which cannot acquire a dilatation suitable to the temperature it receives; we have seen that caloric, in combining with the gases, only raises the temperature because the dilatation meets with an obstacle, (107); hence it results, that the further the air is removed from the state of dilatation which it should have, to be in an equilibrium of temperature, the greater resistance will it oppose to the combination of the caloric, and the more will it lose of its conducting faculty, so that the air which would take the temperature of the surrounding bodies with facility, if it could acquire suitable dimensions under a given pressure, becomes a worse and worse conductor in proportion as it receives a temperature further removed from the dimensions which it can take. The air then experiences an effect which may be compared to that of a body in which the force of cohesion obstructs the action of a liquid, which can effect its solution as soon as this obstruction begins to be diminished.

This explanation is applicable to the conservative property of heat which Rumford has proved to belong to the air which adheres to particles such as those of eider-down: this air only adheres by a true affinity which probably reduces its dimensions, or at least opposes its dilatation; and if the water can drive it off, it is only because

it combines with these substances, or adheres to their surface by its affinity, so that the air will then experience the same effect from the action of the affinity of the bodies to which it is adherent, as is produced on its elastic effort by the space within which it is confined, and in which it receives a higher temperature without having the power to dilate.

Thus the elastic fluids which dilate much more by a similar change of temperature than liquids and solids must have the corresponding faculty of entering more easily into combination with caloric; they offer but little resistance to compression; they heat by the reduction of their volume; and they cool when they dilate: do not these effects announce a great disposition to combine with caloric, or to abandon it, and to receive different degrees of saturation from it? and nevertheless, according to the opinion of Rumford, there must be an insurmountable barrier between the most distant temperatures of the different particles of a gas, when these particles do not meet with a solid body.

It is possible that liquid substances may be much better calculated to conduct heat than when they are in a solid state: the properties of the reciprocal affinity which produces cohesion seem to point this out; for since this affinity opposes the dilatation, it will offer an obstacle to the combination of the caloric: this resistance to its introduction is also proved by the quick accumulation which is made of it as soon as the force of cohesion is destroyed, so that it is opposed to the combination of caloric as well as to that of other substances: in fact, water seems to take the common temperature more easily, independent of the locomotion of its particles, than ice, which is a very bad conductor, and it is perhaps from this difference that ice, and all the solids which pass to the liquid state,

liquefy at the surface instead of taking the common temperature.

I only offer these last explanations as conjectures which may invite to experimental inquiries on a subject which is not indifferent to chemical theory.

NOTE XVII.

THE Citizens Desormes and Clement have advanced,* that if water is passed into a barometer tube in which there is ether, *the elastic force of the latter is prodigiously augmented.*

If ether and water had no action on each other it might be conceived that, when these two fluids were put into a barometer tube together, their vapours would act on the column of mercury, independently of each other; that is to say, that the quantity which the mercurial column would be depressed, would be equal to the sum of the two columns which each vapour could sustain separately in a vacuum, but it cannot be conceived at the same time how two elastic fluids, having a marked action on each other, can, when they are mixed, support a column of mercury greater than the sum of those which they could support separately in a vacuum. If it were so, we could have no precise idea of chemical attraction, since it would be a force which would sometimes bring together the moleculæ of bodies which combine, and sometimes separate them. Besides, the state of composition of the

* Ann. de Chim. Fruct. An. X. p. 303.

substances

substances employed may lead to error; for example, if concentrated pot-ash is mixed with ammonia, there can be no doubt that the elasticity of the ammonia is considerably augmented by the pot-ash, by its acting strongly on the water, and consequently by diminishing its action on the ammoniacal gas. This is exactly what passed in the experiment of Citizens Desormes and Clement. The ether which they used contained alcohol, which diminished its elasticity in the ratio of its volume, and the water which they added increased it in the ratio of its action, which is much stronger on the alcohol than on the ether. The following experiments will prove this explanation.

The centigrade thermometer indicating 15° , and the barometer 76 centimeters, two barometer tubes were taken; into one, sulphuric ether, carefully prepared, was introduced, and into the other, the same ether, but which had been washed with about three times its volume of water. The vapour of the first ether supported a column of mercury of 31.3 cent. and that of the other a column of 35.5 cent.; whence it is already evident, that water as the property of abstracting a principle from the ether which diminishes its elasticity, and this principle can only be alcohol. After this a volume of water nearly equal to that of the contained ether was introduced into each tube, and the elasticity of the unwashed ether was augmented a centimeter, and that of the washed ether only three millimeters, which agrees perfectly with what has been said of the property which water has of taking the alcohol from the ether, whose elasticity was diminished by its action. Besides, it is evident that the elastic force of the water is not entirely added to that of the washed ether, since the reduction of the column of mercury was only 3 millimeters, while at the temperature of 15° it should have been more than a centimeter; this is doubtless

doubtless occasioned by the action between the water and the ether. By adding more water to the two tubes, in such quantity, however, that there might not be enough to dissolve all the ether, the column of mercury was not sensibly affected in either tube; but as soon as the proportion of water was greater than that necessary to dissolve the ether completely, the mercury rose considerably in the two tubes; afterwards, by a new addition of ether, it nearly regained its former level, allowing for the weight of water added. All these facts agree with chemical phenomena, and are clearly explained.

To be more thoroughly convinced that the great augmentation of the elasticity of the ether was owing to the powerful action of the water on the alcohol, another tube was taken, into which a little ether washed with water was at first introduced, which supported a column of 38.5 cent., afterwards a little alcohol was added. The first momentary effect was a depression of 2 millimeters in the column, but by a slight agitation the mercury rose rapidly, so that the vapour of the mixture of ether and alcohol only supported a column of 25 centimeters: water being then introduced, it suddenly lowered the mercury to 5.7 cent.

It seems, therefore, to be completely demonstrated, by the experiments above recited, that the great augmentation of the elasticity of the ether obtained by Citizens Desormes and Clement arose from the impurity of that which they employed. The same experiments also prove, that rectifications carefully made do not free the ether from all the alcohol which it may contain, and that washing it with water, or with such other bodies as act strongly on the alcohol, and but little on the ether, are excellent methods of giving it all the elasticity which is peculiar to it. There need not be any fear that ether thus washed retains a sensible quantity of water; for having distilled it

it by a very moderate heat, preserving only the first portions, its elastic force was only one millimeter stronger than that of ether simply washed.

NOTE XVIII.

LAPLACE, whom I had consulted on the changes which the elasticity of gases experience by their compression, sent me Note V. which I printed immediately: after a more attentive investigation he has given me that which I now insert; it results from it, that what I have said (111—150) must be modified; that the quantities of caloric contained in a gas do not follow the relations of the volumes, independent of the effects of the compression, and that the gases do not differ from liquids and solids with respect to the caloric which they can abandon in one circumstance, and to that which is retained in a greater state of condensation, (121).

" Note V. page 409, having been written in haste, I
" have discovered, since its impression, that it requires
" to be modified; it is not correct to say, that the repul-
" sive force of two neighbouring moleculæ of a gas is
" always the same, at an equal temperature, whatever
" may be the condensation. This force is proportional
" to the temperature, and reciprocal to the mutual dis-
" tance of these moleculæ, or, which is the same thing,
" to the cube root of the volume of the gas in its different
" states of condensation or rarefaction. To prove this,
" let us consider a volume of gas reduced to its eighth
" part by compression: in this new state it will have four
" times as many moleculæ, and consequently four times
" as

“ as many springs applied to a given surface ; thus, since
“ the pressure is eight times greater, it is necessary that
“ the tension of each of its springs should be twice as
“ great; it is therefore reciprocal to the mutual distance
“ of the neighbouring moleculæ, which in this state is
“ only half. The argument which concludes the note
“ cited, connects this general property to that of an
“ equal dilatation in all the gases, by equal augmentations
“ of temperature. It seems, therefore, that there is more
“ heat, in proportion to the volume, in a condensed gas,
“ since the elastic effort of its adjoining moleculæ is then
“ augmented; consequently, if the volume is reduced to
“ one half by compression, less than half the heat which
“ it contained in its first state is disengaged from it,
“ which is conformable to experience and to the velocity
“ observed in sound.”

END OF VOL. I.

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